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CATALYSIS AND CATALYTIC AGENTS IN CHEMICAL PROCESSES.*

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MODERN theoretical chemistry in its conclusions with regard to the structure of atoms and molecules indicates a mode of differentiation of chemical reactions. The mechanism of processes involving ions, oppositely charged, is comparatively simple. It is safe to assume that every time a silver ion meets a chloride ion formation of silver chloride results and in aqueous solution, precipitation ensues when the solution becomes saturated with respect to the salt produced. Reactions between neutral molecules, on the other hand, are by no means so readily initiated nor is the mechanism of reaction so obvious. Even molecules which are oftentimes regarded as "unsaturated" display a marked stability. Ethylene and hydrogen in a clean glass vessel at ordinary temperatures are quite without action on one another. Apparently each molecule under such conditions is a sufficiently stable configuration of negative electrons surrounding positive nuclei that, without special measures, no rearrangement of the electron configurations results. The old method of disturbing the electron configurations of these molecules was to heat the gas mixture. Temperature brings about a more rapid movement of the electrons, positions of instability are more frequently produced, and, conse-

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quently, interaction between the two gases more often occurs. With the aid of a suitable catalytic agent, this effect of increased temperature may be secured at ordinary temperatures. It is only necessary in this case to pass the cold gas mixture over a catalyst composed of nickel obtained by low temperature reduction of nickel oxide. It may be shown that the effect of the nickel is probably to cause, by temporary association of the catalyst with the gas molecules in question, a momentary rearrangement of the electron configuration around the nuclei of the molecules and the consequent production of a higher order of instability in the molecule than normally obtains in the gaseous system, at the given temperature, in the absence of the catalytic agent.

The rôle of the catalyst, therefore, is mainly in that realm of reactions occurring between non-ionized molecules. A moment's thought will show that this includes practically all types of chemical reactions. The ionic reactions are the least affected by catalysts though, even in such, catalytic influences have been found. The influence of the solvent medium is possibly catalytic. Attention may be drawn by way of example to the catalytic influence of manganese sulphate in various titrations with potassium permanganate. The possibilities of the use of the catalyst are legion, on the other hand, in gas reactions, involving oxidation, reduction, halogenation, in the reactions of organic chemistry, hydrolysis and dehydration, substitutions, hydrogenations, dehydrogenations and oxidations whether homogeneous or heterogeneous, in gas-solid and gas-liquid systems. The accelerating influence of manganese dioxide on the decomposition of potassium chlorate shows, too, that one solid may markedly influence the reactivity of another solid. Certain electrochemical processes involving cathodic or anodic reactions are modified as to rate by the presence of catalytic agents. The activity of the enzymes in biochemical processes is also frequently catalytic in nature. Finally radiation, in one or another of its varied forms, whether as light, ultra-violet, visible or infra-red, or as X-rays or as the radiations from radioactive materials, may also function in a catalytic manner.

In all such processes the rôle of the catalytic agent is that of an intermediary, accelerating, or in some cases retarding, the operation of reactions which would normally occur, though at differing rates, in the absence of the catalyst. The accelerating or positive catalysts are those with which the chemist is normally

concerned. Occasionally, as in the use of such a substance as acetanilide to stabilize hydrogen peroxide solutions, negative catalysts or retarding agents are utilized. In certain reactions one of the reacting substances or one of the products of the process is a catalyst for the original reaction. Such cases are termed autocatalysis. Thus the decomposition of silver oxide to yield oxygen and silver is catalyzed by the finely divided metallic product. A reaction which may be initially quite slow will in such cases gather momentum as the autocatalyst is produced.

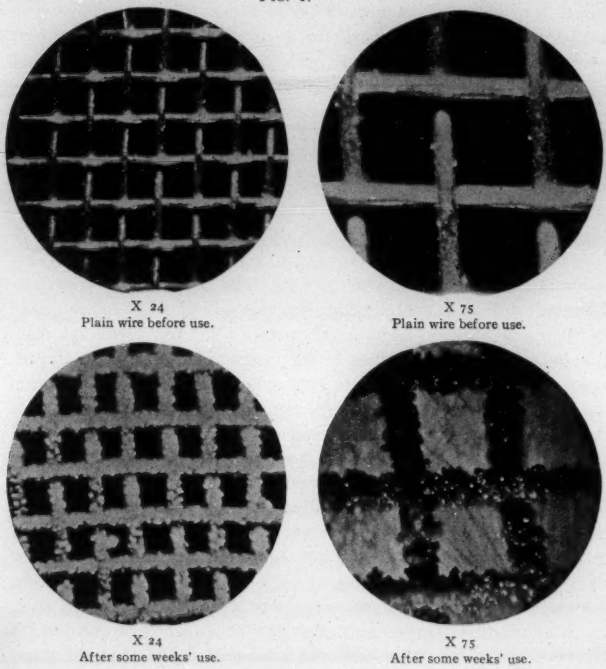
The modification of reaction rate which a true catalyst produces must be attained without change in the chemical form of the catalyst on completion of the reaction cycle. Its participation in the process as an intermediate compound is not excluded; indeed, for many homogeneous catalytic processes it seems necessary to assume the formation of such intermediate compounds. Nevertheless, a true catalytic agent must be regenerated in its original chemical form when the catalytic operation is complete. This being so, it is evident that catalysts will also be characterized by their operation in small concentrations for promotion of reaction between large quantities of the interacting substances. Thus, some recent figures [1] indicate that one square inch of platinum gauze, 0.003 wire and 80 mesh, acting as a catalyst in the oxidation of ammonia, gives a yield of six pounds of nitric acid per day. For the present, also, it seems safer to assume that the catalyst promotes the establishment of the same equilibrium as would normally prevail in the absence of a catalyst. It is true that this viewpoint has been vigorously contested from several quarters in recent years. As yet, however, no unequivocal case of a shift in equilibrium caused by a catalyst has been brought forward, while there are many cases in which the reverse is true.

While the catalyst remains unchanged chemically on completion of the process, the same does not hold true in its physical state. Indeed, in many cases of heterogeneous catalytic reactions the solid catalyst shows marked physical change. The active catalyst is normally a porous, amorphous material and, in process of activation, catalysts tend to assume this form. Manganese dioxide, originally coarsely crystalline, will be found to be an amorphous powder after having catalyzed the decomposition of potassium chlorate. The change is most strikingly manifested in the micro-

[1] Private communication from Dr. Chas. L. Parsons.

scopic examination of platinum gauze before and after use in the oxidation of ammonia. The gauze is converted from a smooth plane-surfaced wire to a corrugated pitted material. This is shown in the accompanying figure. Similar changes in physical

FIG. 1.



X 24
Plain wire before use.

X 75
Plain wire before use.

X 24
After some weeks' use.

X 75
After some weeks' use.

form are shown by silver gauze when used for the catalysis of hydrogen oxygen mixtures.

Principles and Methods of Catalytic Investigation.—There appears to be a fairly general impression that the investigation of a catalytic process is a somewhat random occupation and that the discovery of a catalytic agent is a fortuitous result of trial and error with indiscriminate selections from available compounds. It is true that a large number of catalysts have been discovered

accidentally, or rather with little basic theory guiding the choice of material to be studied. With accumulation and systematization of facts relative to catalytic agents and the reactions they promote, the study of new processes becomes, however, less and less empirical. In the early days of organic chemistry, the student of a new compound doubtless applied such reagents as sulphuric acid or strong alkali quite empirically in the hope that he might gain the desired information relative to his material. To-day, as a result of accumulated experience he applies these and other catalytic agents consciously, with full knowledge of the normal reactions which they promote. In the same way, the coördination of knowledge in reference to catalytic agents and the reactions they assist gives to the catalytic chemist of to-day more deliberate and purposeful methods of work. A glance at the subjoined

Reaction Process	Type of Catalyst	Exemplification in Industrial Practice.
Hydration and Hydrolysis	Acids	(a) Hydrolysis of glycerides, soap and candle industry, sulphuric, sulphonic (Twitchell reagent) acids as catalysts. (b) Hydrolysis of starches and wood cellulose to yield sugars. Sulphuric, hydrochloric, sulphurous acids as catalysts. (c) Hydrolysis of esters using acids. (d) Hydration of acetylene to yield acetaldehyde. Various acids as catalysts.
	Alkalies	(a) Hydrolysis as in (a) and (c) above. NaOH, KOH, $Ca(OH)_2$, MgO, ZnO as catalysts.
Dehydration	Acids	(a) Manufacture of ether. Sulphuric, sulphonic and phosphoric acids as catalysts. (b) Esterification processes. Hydrochloric and sulphuric acids as catalysts.
	Oxides	(a) Manufacture of ethylene and unsaturated hydrocarbons. Clays, Al_2O_3, SiO_2, TiO_2 as catalysts.
Halogenation	Non-metallic elements	(a) Chlorination of carbon disulphide, carbon monoxide and hydrocarbons. Carbon, iodine, sulphur as contact agents.

	Chlorides	(a) In synthetic organic chemistry. $AlCl_3$, $FeCl_3$, $SbCl_5$, $SnCl_4$, $ZnCl_2$, $HgCl_2$, as contact agents.
Oxidation	Metals, especially the platinum metals	(a) Contact sulphuric acid process using finely divided platinum on a suitable support. (b) The oxidation of ammonia using a platinum gauze. (c) The preparation of formaldehyde, using copper or silver (see dehydrogenation).
	Oxides	(a) Lead chamber process, employing a gaseous catalyst, oxides of nitrogen. (b) Contact sulphuric acid manufacture with iron oxide catalyst. (c) Chance-Claus process of sulphur recovery. Oxide of iron as catalyst. (d) Purification of illuminating gas. Hydrated oxide of iron as catalyst. (e) Surface combustion processes, refractory oxides as catalysts. (f) Oxidation of hydrocarbons, V_2O_5, MoO_3, WO_3, etc., as catalysts.
	Salts	(a) Deacon chlorine process, copper chloride as catalyst. (b) Oxidation processes in the dye industry. Mercury and copper salts. (c) Oxidation of aldehydes, manganese salts as catalysts. (d) Drying of oils. Metallic soaps as accelerators.
Hydrogenation	Metals	(a) Hydrogenation of oils. Nickel and platinum as contact agents. (b) Fine organic chemical industry, *e. g.*, synthesis of cyclo-hexane, reduction of organic compounds. Nickel as catalyst.
	Oxides	(a) Hydrogenation of oils, nickel oxide as catalyst (especially at elevated pressures).
Dehydrogenation	Metals	(a) Cracking of oils, nickel, copper, iron, aluminium as catalysts.

		(b) Dehydrogenation of alcohols, copper, silver and nickel as catalysts.
	Oxides	(a) Cracking of oils, Al_2O_3 and TiO_2 as catalysts. (b) Dehydrogenation of alcohols, ZnO, SnO, CaO and MgO as catalysts.
Nitrogen Fixation	Metals and metal-oxide mixtures	(a) Ammonia synthesis. Reduced iron, iron-molybdenum, iron-potash, and nickel-sodium as contact agents. (b) Cyanide formation. Reduced iron as catalyst. (c) Arc process of oxide of nitrogen formation. Metal electrodes as negative catalysts. (d) Nitride formation (Serpek process). Iron, copper, chromium, molybdenum, etc., as catalysts.

table of the more important industrial catalytic reactions classified as to type of reaction and as to type of catalyst employed will suggest the method of attack upon a new catalytic problem. It will be clear that the first stage in the investigation is a determination of reaction type, whence the probable type of catalyst will follow. The trained catalytic chemist would spend little time investigating a hydrogenation process using catalysts which normally catalyze say halogenation or dehydration. Each class of reaction has its own class of catalytic agent and each of these classes may similarly be circumscribed as to members. Thus, for example, it may be seen that as catalysts for oxidation processes, oxides are an important class of catalysts. Of the oxide class, however, it is remarkable that only a limited number function at all prominently as catalysts. The oxides of well-defined stability are conspicuously absent. The oxides of the alkali metals, to a less extent those of the alkaline earths, definite irreducible oxides such as magnesium oxide and aluminium oxide are not frequently to be found among the oxide catalysts of oxidation. On the other hand, the labile oxides such as those of iron, copper, manganese, silver, vanadium, tungsten, molybdenum uranium, chromium, cobalt and cerium are frequently to be noted in a systematic study of such oxide catalysts of oxidation. In view of what has been said with regard to the catalyst as promoter of electronic instability in the reacting molecules, it is

interesting to observe that this large class of catalytic agents is made up of compounds of elements which all show a ready tendency to modify the configuration of electrons surrounding their positive nuclei. In the older nomenclature they are the oxides of polyvalent metals. It is undoubtedly due to this variability of electronic configuration that their oxidation activity is due. In a similar manner other types of reaction and other classes of catalysts may be treated. The result of such considerations is a studied and orderly choice of reaction catalysts.

It is advantageous, also, to remember that, in normal circumstances, a catalyst accelerates both the forward and the backward reactions of an equilibrium process. The catalyst of hydrogenation should therefore be, and is, frequently, the catalyst of dehydrogenation processes. Nickel assists the direct hydrogenation of benzene; it is also the catalyst for the dehydrogenation of cyclo-hexane. Since it has been observed, in the reduction of nitrobenzene by hydrogen in the presence of nickel, that reaction may proceed further than the aniline stage and yield benzene and ammonia, it naturally suggests itself to the catalytic chemist that nickel will catalyze the removal of hydrogen from benzene and ammonia to yield aniline. This has been shown to be true,[2] though the yields attained are exceedingly small.

Correct appreciation of such principles and suitable correlation with known facts frequently results in the forecasting of suitable catalytic agents. There is at the present time in the development stage a catalytic process of immense industrial potentialities, concerning which details are as yet carefully withheld. The process involves the treatment of water-gas ($H_2 + CO$) with catalytic agents to yield methyl alcohol. The reaction may be formulated by means of the equation

$$CO + 2H_2 = CH_3OH.$$

The process probably takes place through formaldehyde as an intermediate product which is then immediately hydrogenated to methyl alcohol.

$$CO + H_2 = HCHO.$$

$$HCHO + H_2 = CH_3OH.$$

The essential reactions are hydrogenations and call therefore in

[2] Meyer and Tanzen, Ber., **46**, 3198 (1913).

all probability for reduced metals as catalysts. The knowledge that nickel, cobalt and palladium cause the hydrogenation of carbon monoxide to proceed to methane and water

$$CO + 3H_2 = CH_4 + H_2O$$

seems to rule these catalysts out of court in the reaction under consideration. The knowledge that copper and platinum are incapable of promoting the conversion of carbon monoxide to methane brings them therefore prominently into consideration. The knowledge that copper is an active agent for the dehydrogenation of methyl alcohol to yield formaldehyde is additional evidence in favor of a trial of reduced copper as the catalyst. The information which would permit a test of such a forecast has not been disclosed but it should not long be delayed.

A prior knowledge of the equilibrium conditions in the reaction to be catalyzed is an extremely valuable asset to the catalytic investigation. The technical success that has been attained in the contact sulphuric acid process, in the synthesis of ammonia and in the water-gas catalytic process of hydrogen manufacture for ammonia synthesis is based, in no small measure, on the equilibrium data accumulated by the Badische Anilin and Soda-Fabrik and associated investigators. These data define the optimum working conditions and facilitate the definition of working efficiencies. These processes are at once classical examples of the contributions of catalysis to modern chemical industry and justification of the claims of theoretical science upon the support of the technical man.

In the absence, however, of exact equilibrium data, useful approximations may be made. The Nernst approximation[3] formula is especially useful and applicable. Nor can the conclusions of thermodynamics be neglected by the catalytic chemist in the definition of the operating conditions. Thus, in the reaction already discussed,

$$CO + 2H_2 = CH_3OH$$

the reaction is exothermic. Low temperatures therefore favor the formation of methyl alcohol. Pressure facilitates its production in higher concentration at a given temperature. The

[3] See Lewis, "System of Physical Chemistry," vol. ii, 1919, pp. 75 and 330, *et seq.*

upper limit of temperature for economically feasible yields may be computed with the aid of the approximation formula of Nernst.

The Form of the Catalyst; Catalyst Support Materials.—In homogeneous media the form of the catalyst is not important. A gaseous catalyst in a gas reaction or a dissolved catalyst in liquid systems has a definite and readily reproducible form. In the last analysis the acceleration or retardation caused by the catalyst is, in such systems, proportional to its concentration. This point is not infrequently forgotten owing to deviations from strict proportionality between reaction velocity and presumed concentration. Thus, as is well known, the catalytic action of acids in hydrolytic processes is not strictly proportional to the molar concentration of the acid catalyst. Such abnormalities have been the object of much study. Better concordance is obtained between hydrogen ion concentration and catalytic activity, but even there the proportionality is not an exact one. Various reasons for this fact have been adduced, none completely satisfactory. By some it is urged that the undissociated acid molecule is catalytically active; by others that only non-hydrated hydrogen ions are catalytically active. Others define the catalysis in terms of the thermodynamic "activity" of the ions. Concerning all such, whatever the real explanation, it may be remarked that the catalysis in homogeneous media will be proportional to the active mass of the actual catalyst or catalysts, since there may be several present.

If the catalytic reaction be heterogeneous, the form of the catalyst becomes immediately a matter of first importance. That this is so in liquid-liquid systems may be shown in reference to hydrolytic processes. In homogeneous media it is well known that the reaction velocity of hydrolysis of esters is approximately proportional to the hydrogen ion concentration. In heterogeneous systems, however, the acid strength is not the principal factor. Thus, hydrochloric acid is not so good an agent for the splitting of fats as the sulphonic acids, though these acids are approximately of equal strengths. The activity of the sulphonic acids is modified profoundly by the nature of the hydrocarbon grouping, as was early shown by Twitchell. The Twitchell reagent, naphthalene-stearo-sulphonic acid or a similarly constituted acid, undoubtedly owes its efficiency as a hydrolytic

agent in the splitting of fats to the fact that the molecule of acid catalyst is orientated, so that the polar sulphonic grouping is in the aqueous medium, while the hydrocarbon nucleus is within the glyceride oil. This is a splendid instance of technical development far in advance of scientific theory. It will be seen that the concept of orientation of molecules as a necessary feature of contact action is of quite recent origin.

In the case of solid contact agents, the problem of form is equally important. The striking feature common to most of the contact catalysts is their porous or finely divided structure. The successful contact agent is characterized by this amorphous nature of the material. As already emphasized in this connection, with platinum and silver gauze catalysts, the preliminary phase of activation is accompanied by a change in the surface form of these metals to a roughened surface with which catalytic activity is high. This change may operate favorably to catalysis in two ways. It may change the normal spacing of the atoms in the metal surface to one more favorable for the adsorption of the reacting gas molecules in such configurations as are conducive to interaction. In addition, however, the activation may result in the production of a larger number of atoms in the surface layer, with electrons in a more or less unsaturated or free condition unshared by neighboring atoms and able, therefore, to enter into association with impinging molecules more readily than the symmetrically placed atoms in a non-catalytic surface. Evidence of this phenomenon is forthcoming from adsorption experiments[4] with catalytic agents in the Princeton laboratories. Nickel obtained by reduction at low temperatures (200–300° C.) shows high absorption for many gases. The extent of adsorption, however, is determined largely by the previous history of the catalyst. By submitting the catalyst to temperatures between 300–600° C. the nickel will slowly lose its adsorptive power, presumably by saturation of the free electrons of the nickel atoms with neighboring nickel atoms, which process is, of course, the phenomenon of crystallization. It is undoubtedly this same phenomenon which accounts for the slow loss of activity of a catalyst with prolonged use, even though reactants of the utmost purity be used.

The loss of adsorptive power by nickel, parallels the variation

[4] See Taylor and Burns, *Journ. Amer. Chem. Soc.*, **43**, 1273 (1921).

in catalytic power of this metal with variation in temperature of preparation. Kelber [5] showed that nickel oxide *per se*, when reduced at about 300° C., gave a moderately active catalyst, but when reduced at 450° C., gave a product of but feeble activity. The conclusions have recently been checked by Armstrong and Hilditch, who show that reduction at higher temperatures gives rise to considerable shrinkage in the volume of the catalyst.

This shrinkage and loss of catalytic activity can be largely suppressed if the active material is spread upon an inert support. In this way, for example, it is possible to produce at 500° C. a nickel catalyst supported upon kieselguhr, of greater activity than from precipitated nickel hydroxide, by reduction at 300° C. The kieselguhr, which does not shrink on heating, almost wholly determines the bulk of the product and the nickel adhering to the support can only coalesce with much greater difficulty. The factors in these several cases are well set forth in the following chart, due to Armstrong and Hilditch:

Source of Reduced Nickel			Reduced Nickel		
Density	Apparent Volume c.c.	Temperature of Reduction	Density	Apparent Volume c.c.	Catalytic Activity
Powdered fused oxide 6.96	0.35	500° C.	8.14	0.52	None
Precipitated hydroxide 5.41	0.87	(300° C.)	7.85	0.83	Fair
		(500° C.)	8.18	0.56	Very little
On kieselguhr 1.63	3.22	500° C.	1.85	2.67	Very active

Recent measurements by Mr. A. W. Gauger in the Princeton laboratories have shown that the adsorption of nickel, *spread on kieselguhr*, is the same when the catalyst is reduced at 500° C. as when reduction is effected at 300° C. in sharp contrast to the behavior of "unsupported" nickel. Concordance is, therefore, shown between these adsorption measurements and the catalytic studies of Kelber, Armstrong and Hilditch. It has been shown, further, that the extent of adsorption of gas by unit weight of metallic catalyst is enormously increased when the catalyst is spread on a porous support. Thus, one gram of nickel spread on diatomite (Nonpareil) brick adsorbs the quantities of hydrogen listed in the tables below, where also are to be

[5] Ber., **49**, 55, 1868 (1916).

found corresponding figures for nickel obtained by reduction of coarsely powdered nickel oxide, prepared by ignition of the nitrate.

Catalyst	C.c.s Hydrogen Gas Adsorbed per gram Ni, at							
	25°	80.5°	175°	184°	200°	218°	250°	305° C.
Nickel without support	0.69	0.63	....	0.53	....	0.48	....	0.36
	....	....	5.2	....	5.1	....	4.73	....

Our researches have enabled us to show also a striking parallelism between adsorptive capacity and catalytic activity in a variety of cases, though this is not the only factor involved, as will later be shown. Nevertheless, the results obtained, and those cited previously, demonstrate the important part which the catalyst support material may play in successful catalysis. With expensive catalytic agents, as, for example, platinum, the use of a support is frequently indispensable.

A variety of materials has been employed as catalyst supports. Platinum is normally employed in the contact sulphuric acid process, either on asbestos fibre or on calcined magnesium sulphate, the platinum being generally sprayed in the form of the chloride on the suitably prepared mass. Mention may also be made of pumice, glass wool, silica fibres, fibrox, various porous siliceous materials such as fireclay, alundum, unglazed porcelain, kieselguhr either in powder form or bonded into brick, charcoal, various porous oxides and anhydrous salts. It is interesting to record metallic aluminium as the most recent of catalyst support materials, now being employed as a support for metallic oxides in the air oxidation of hydrocarbons [6] and in the catalytic conversion of acetic acid to acetone,[7] using lime as catalyst. The metal support facilitates thermal equilibrium in the catalyst system. It is employed in a granular form, obtained by allowing the molten metal to cool slowly in trays, the mass, meanwhile, being vigorously shaken.

Theories of Catalytic Action.—For catalysis in homogeneous systems the intermediate compound theory appears to be generally applicable. The activity of water vapor in gas reactions may be attributed generally to a cycle of changes into which the water molecule enters and in which it is finally regenerated. In

[6] The Barrett Co., Edgewater, N. J.

[7] Stockholms Superfosfat Aktiebolaget, Br. Pat., 1921.

the lead chamber process of sulphuric acid manufacture a cycle of reactions is postulated for the oxides of nitrogen employed as catalyst. It must be observed that even in such media the possibility of heterogeneity cannot be totally excluded. Water vapor is frequently assumed to act as nucleus in such changes. Williamson's explanation of the function of sulphuric acid in the etherification of alcohol, in which ethyl hydrogen sulphate is an intermediate stage, was the first formulation of the intermediate compound theory in homogeneous liquid systems. It is now generally assumed that most homogeneous catalytic reactions occur thus by stages, and stoicheiometric relationships between reactants and catalysts can normally be postulated in such cases.

Whilst the intermediate compound theory gives the mechanism by which the reactions occur, it gives no indication at all as to why such successive reactions occur with enhanced rapidity. The radiation theory of chemical action, whereby the necessary energy of reaction is assumed to be absorbed from the thermal radiation of the system in quanta of definite frequency or frequencies, has been recently applied not only to ordinary thermal reactions, but has also been extended to such homogeneous catalytic reactions.[8] One of the recent experimental contributions to this theory has been obtained by H. A. Taylor in Liverpool, England, with reference to the influence of solvent on the reaction velocity. It has been shown that the critical increment of energy, as deduced from the temperature coefficient of reaction velocity, required for the decomposition of triethyl sulphine bromide in nitrobenzene solution, corresponds to a radiation frequency 3.0×10.4 or a wave-length of 1.0μ. Experimental measurement of the infra-red absorption of the bromide in nitrobenzene shows a distinct bend at 1.05μ in good agreement with the theory. Other measurements with other solvents give further support to the observation that the source of necessary energy is the temperature radiation of the system, communicated in terms of a single quantum corresponding to a given frequency or in terms of a small number of quanta of correspondingly lower frequency. The experiments of Daniels and Johnston[9] unquestionably lead to the conclusion that the absorption of energy may occur by means of several quanta as opposed to a single quantum.

[8] See Lewis, *Journ. Chem. Soc.*, 1914-1920; *Trans. Farad. Soc.*, Sept., 1921.
[9] *Journ. Amer. Chem. Soc.*, **43**, 72 (1921).

Attempts have been made to prove the influence of infra-red radiation as an accelerator of reaction by Rideal and Hawkins [10] and by Nil Ratan Dhar.[11] In the former case, experimental error alone will account for all the observed effects of infra-red radiation. The claims of Dhar with reference to sucrose solutions have been negatived by experiments in the Princeton laboratories, as well as by experiments of Lindemann and Taylor in Oxford.[12] It has been shown also by Taylor,[13] and by Lewis and McKeown,[14] that the net result of photochemical infra-red radiation of a solution in bulk must be very small, owing to the high *extinction* coefficient of such solutions for infra-red radiation. The thickness of radiated solution is in most cases confined to a small fraction of a millimetre. Further work in this field should be directed to gas reactions.

For heterogeneous catalytic reactions, the adsorption theory of catalysis has recently received extended experimental test, so that a much clearer picture of reaction processes is now obtainable. Faraday postulated adsorption of hydrogen and oxygen at the surface of a platinum plate to account for the velocity of reaction between these gases at such a surface. The kinetic studies of Bodenstein and his co-workers led Bodenstein and Fink to assume that rate of reaction was determined in many cases by the rate at which the reacting gases could penetrate through a layer of adsorbed gas to the active surface. In this way, the retarding effect of sulphur trioxide on the combination of sulphur dioxide and oxygen at a platinum surface was explained. Langmuir's studies of the reactions of gas molecules at low pressures in contact with metallic filaments, and his studies of oil films on water surfaces, have indicated the existence in such cases of stable adsorbed films, monomolecular in extent, with the molecules oriented on the surface in definite manner. The relative stabilities of such monomolecular layers on the given surface are shown by Langmuir to determine the form of reaction equations obtained in such surface reactions.

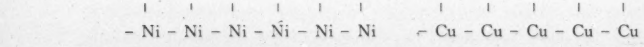
The specificity of catalytic agents in respect to adsorption of

[10] *Journ. Chem. Soc.*, **117**, 1288 (1920).
[11] *Zt. Anorg. u. Allgem. Chem.*, 1921.
[12] *Nature*, **1921**.
[13] *J. Ind. Eng. Chem.*, **13**, 75 (1921).
[14] *J. Amer. Chem. Soc.*, **43**, 1288 (1921).

gases is well illustrated by the measurements of Taylor, Burns and Gauger in experiments with hydrogenation catalysts. Nickel, the most important of such agents, shows marked adsorptive capacity for hydrogen, carbon monoxide and ethylene. Copper, on the other hand, adsorbs carbon monoxide and ethylene to a more pronounced degree than hydrogen, though this latter is measurably adsorbed. As was pointed out, however, by Taylor and Burns,[15] the variation in adsorptive capacity of the agents is alone insufficient to account for the variation in catalytic activity. All of the metals listed in the subjoined table show measurable adsorptions of the reacting gases in the reactions listed. They display, however, the marked divergencies, as catalysts, which are noted in the table.

Reaction	Catalysts	Non-catalytic
$CO + 3H_2 = CH_4 + H_2O$	Ni, Co, Fe, Pd.	Cu, Pt.
$2CO = CO_2 + C$	Ni, Co, Fe.	Cu, Pt.
$C_6H_6 + 3H_2 = C_6H_{12}$	Ni.	Cu.

It is possible in many such cases that orientation of the adsorbed molecules may be shown to account for such specificity. The orientations postulated in the appended examples might be adduced to account for the activity of nickel and the non-activity of copper in the decomposition of carbon monoxide to carbon dioxide and carbon.



It must be pointed out that such postulates entirely lack experimental confirmation, and, indeed, the idea of a CO molecule, attached to copper and to platinum by the oxygen molecule, is in disagreement with the views expressed by Langmuir [16] in this regard as a result of his studies of the interaction of carbon monoxide and oxygen in presence of platinum.

Orientation of the molecules of dissolved substances at charcoal surfaces is held by Kruyt and Van Duins [17] to account for

[15] *Loc. cit.*

[16] *Trans. Faraday Soc.*, Sept., 1921.

[17] *Rec. Trav. Chim.*, [4], **2**, 249 (1921).

the variability in the action of charcoal suspended in various liquid systems. Both methyl acetate and sodium hydroxide are adsorbed from aqueous solution by charcoal. No acceleration of reaction velocity is thereby obtained. On the contrary, a retardation results. Charcoal, however, accelerates the interaction of potassium iodide and β dibropropionic acid, because, in agreement with surface tension measurements, the reactive groupings of these substances are brought into close contact on the charcoal surface.

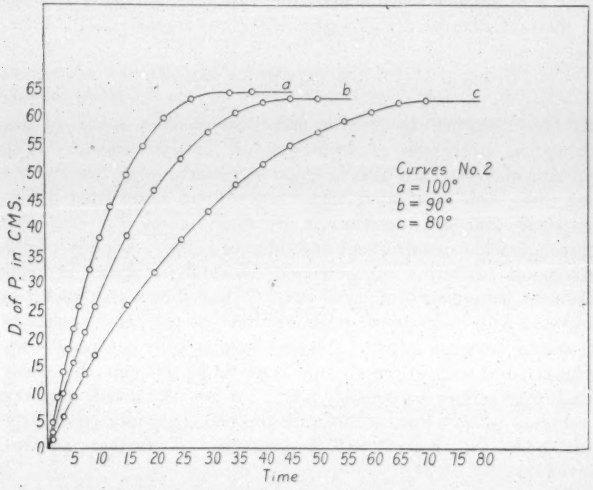
Convincing proof of the divergence between the adsorption of gases by metallic catalysts and by porous inert adsorbents has been obtained by Taylor and Gauger in a study of the adsorption isotherms of hydrogen on catalytic nickel. The experimental data are also in good agreement with Langmuir's view that such adsorption layers are seldom more than monomolecular and are determined in many cases by electronic rearrangements of adsorbent and adsorbed gas. A study of the adsorption isotherms of hydrogen on catalytic nickel at temperatures between 25° C. and 305° C. has shown that nickel is saturated with hydrogen at relatively low gas pressures. Already at 40-mm. pressure at 25° C., nickel is completely saturated with hydrogen and with increase of pressure up to 760 mm. the extent of adsorption does not sensibly alter. At 305° C. it only requires a pressure of 275 mm. to saturate the nickel surface completely with hydrogen, beyond which pressure no further adsorption occurs.

'Furthermore, if the minimum pressures, beyond which further increase of pressure does not produce additional adsorption, be regarded as the saturation pressures of a surface nickel-hydrogen complex at the several temperatures, an interesting conclusion may be drawn. It is found that the logarithms of such "saturation pressures" plotted against the reciprocal of the absolute temperatures yield a straight-line relationship, as would vapor pressures or dissociation pressures under similar treatment. From the slope of this straight line it is possible to determine the magnitude of the thermal quantity involved in the disruption, and, therefore, in the formation, of such a surface complex. In the case of nickel and hydrogen under consideration this has been shown to be of the order of 2500 calories per mol of hydrogen adsorbed. An alternative experi-

mental check on this magnitude is now being sought, since another, though less certain, method used by Rideal [18] to determine this magnitude gives a value of 12,000 calories.

The significance of such adsorption isotherms in the problem of reaction kinetics at a catalyst surface may also be emphasized.

FIG. 2.



It is obvious that, if reaction occurs only with measurable velocity at the catalyst surface and in proportion to the concentrations of the reacting gases at such surfaces, the equation will be dependent upon the nature of the adsorption isotherms of the reacting gases. For example, in the reaction yielding hexahydrobenzene,

$$C_6H_6 + 3H_2 = C_6H_{12}$$

the ordinary stoicheiometric equation would require the reaction to be proportional to the cube of the partial pressure of the hydrogen gas. Since, however, the concentration of hydrogen at a nickel surface is independent of the hydrogen gas pressure

[18] *Jour. Chem. Soc.*, **121**, 309 (1922).

over a considerable range of pressure (above 100 mm. at 100° C.) it might be anticipated that in the catalytic hydrogenation of benzene the partial pressure of the hydrogen above 100 mm. would have little or no influence on the rate of reaction, provided always that the other gases and vapors present in no way seriously modified the hydrogen adsorption. That such is the case is to be inferred from the initial straight-line nature of curves obtained by Taylor and Dougherty in a kinetic study of the above reaction at 80°, 90° and 100° C. It is impossible to obtain such straight-line relationships for the rate of reaction on any theory which assumes that the hydrogen is acting in proportion of the cube of its partial pressure.

More recent work on the hydrogenation of ethylene in presence of metallic copper by Dr. R. N. Pease, at Princeton, shows, however, that the simple theory, based on adsorption measurements of the single gases at various partial pressures, is not adequate in all cases for the deduction of the kinetics of a reaction in the presence of a catalyst medium. The modifying effects of the other gases present may alter the conclusions. For this reason, adsorptions by a catalyst from mixed gases deserve thorough study.

An interesting phase of the general subject of catalysis is that of preferential catalysis. It is possible, by suitable choice of a catalytic agent, to secure the preferential progress of a given gas reaction in presence of other gases which are also capable of undergoing the same reaction. A familiar example is the preferential oxidation of hydrogen sulphide to sulphur and water

$$2H_2S + O_2 = 2H_2O + 2S$$

in presence of other gases, such as carbon monoxide, hydrogen and methane. This is secured in the purification of illuminating gas by passage of the gas admixed with small quantities of air over a reactive hydrated oxide of iron as, for example, bog iron ore at ordinary temperatures. Another important example of recent industrial development, is the Harger-Terry process of preferential combustion of carbon monoxide with oxygen in presence of hydrogen, a process which has now been applied to the elimination of small quantities of carbon monoxide from hydrogen prepared by the steam-iron process.

A study of the mechanism of this process of preferential

combustion from the standpoint of adsorption has recently been made at Princeton by Dr. A. F. Benton. The normal agencies for such preferential catalysis are certain metallic oxides, preferably obtained by precipitation of the hydroxides and low temperature removal of the water. Among the more important of such oxides are those of copper, iron, manganese and cobalt. Experimental test has shown, in all such cases, that the oxides adsorb carbon monoxide to a very considerably greater extent than they adsorb hydrogen, which, in most cases, is only taken up by such oxides to a negligible extent. It is clear, therefore, why, even when the carbon monoxide is present in small percentages in hydrogen, its reaction at the oxide surface preponderates over that of the hydrogen gas.

A detailed study of the kinetics of such combustion processes at the surface of these oxides on their reduction products has indicated the diversity of the problems involved in such catalytic study. The mechanism of catalysis in the case of hydrogen and oxygen on the one hand, and of carbon monoxide and oxygen on the other hand, may be totally distinct. This is clearly demonstrated in work carried out in collaboration with Dr. R. N. Pease and Dr. H. A. Jones. In contact with copper oxide the measurements indicate that catalysis is determined in each case by alternate reduction and oxidation. In presence of reduced copper, the combination of hydrogen and oxygen is apparently also dependent on alternate oxidation and reduction. With metallic nickel this is certainly not the case. Reaction at nickel surfaces is apparently the oxidation of hydrogen adsorbed on the nickel, a reaction which occurs freely, in presence of an active catalyst, at room temperatures. With carbon monoxide and oxygen in presence of reduced copper, the reaction is similar to that with hydrogen and oxygen in contact with nickel and in marked contrast to that obtaining with these latter gases and copper. The mechanism is certainly not an alternate oxidation and reduction but an oxidation of adsorbed carbon monoxide by oxygen, in agreement with the high adsorptive capacity of copper for carbon monoxide and its low capacity for both hydrogen and oxygen. With suitably prepared copper, carbon monoxide and oxygen will react rapidly at 0° C.

Reactions at Boundaries of Phases and the Problem of Promoter Action.—A study of the reduction of copper oxide

by hydrogen [19] and by carbon monoxide at moderate temperatures (100–150° C.) has demonstrated the importance of the interface between two phases and the chemical activity which may be located at such points. It has been shown that low temperature reduction of copper oxide by hydrogen or carbon monoxide is negligible until copper nuclei are established in the copper oxide mass. Subsequent reaction is then confined to the boundaries between the copper and copper oxide as can be demonstrated visually by the ever-increasing area of the red copper extending outwards from the original nuclei. The amounts of water vapor and carbon dioxide produced per unit of time as a result of such reduction processes increase steadily with increasing extent of interface; they attain a maximum and then steadily diminish as the reduction of the oxide is completed. The form of such a time-reaction curve is typical of an autocatalytic process. It evidently finds its explanation in the higher order of reactivity of an oxide ion when situated adjacent to a neutral copper atom which is also capable of adsorbing hydrogen, probably in the atomic condition, and also carbon monoxide.

This example of activity at an interface is another case of a variety of such phenomena recently indicated by Langmuir.[20] Faraday observed that a perfect crystal of sodium carbonate or sodium sulphate refuses to effloresce until the surface is scratched or broken and that the efflorescence then spreads from the injured place. Prof. G. A. Hulett has frequently drawn the writer's attention to the similar behavior of hydrated cadmium sulphate which is readily obtained in large and perfect crystals, which maintain a constant weight in a desiccated space until a boundary between a hydrated and a dehydrated phase is established. Langmuir has similarly shown that in the dissociation of calcium carbonate by heat, the carbon dioxide is produced only at the boundary between the calcium carbonate and the calcium oxide phases. The dissociation of silver oxide to yield oxygen and silver, studied by G. N. Lewis,[21] is a parallel case, it being observed that the rate of dissociation increased with increasing production of silver. Silver was termed the autocatalyst of the reaction. Undoubtedly the presence of neutral silver atoms with

[19] Pease and Taylor, *J. Amer. Chem. Soc.*, **43**, 2179 (1921).
[20] *Trans. Farad. Soc.*, Sept., 1921, *Jour. Amer. Chem. Soc.*, **38**, 2263 (1916).
[21] *Zt. Phys. Chem.*, **52**, 310 (1905).

their free electrons affects the stability of the adjacent oxide ion. Lewis demonstrated the analogy existing between the silver oxide decomposition and the growth of crystals in a saturated solution in which, as is now well known, forces electronic in nature are involved. The different nature of the dissociation process when such interfaces are not set up is well illustrated in the case of mercuric oxide dissociation studied by Hulett and G. B. Taylor.[22] In this case at temperatures where dissociation becomes marked (500° C.), the mercury formed is also vaporized. No interface results and so no acceleration of the dissociation is obtained. As a result, passage of nitrogen gas for twenty-four hours over pure mercuric oxide at 500° C. gave concentrations of oxygen corresponding to only a few mm. pressure, whereas the true equilibrium pressure at that temperature was upwards of one atmosphere. When interfaces were produced by the addition of foreign substances, iron oxide, manganese dioxide and platinum, true equilibrium pressures were at once established, measurable both statically and dynamically. The recent researches of Kendall and Fuchs[23] on the accelerated decomposition of silver oxide, mercuric oxide and barium peroxide in presence of other oxides is also illustrative of the effect produced by the deliberate creation of interfaces. The view expressed by Kendall and Fuchs that the added oxide influences also the dissociation pressure of the oxide has not, in the view of the writer, been unequivocally demonstrated. That the rate of decomposition is accelerated is, however, unquestionable.

Enhanced activity at an interface is certainly more common than even the examples already given would indicate. A search of the literature is constantly yielding fresh material in which experiment shows abundant evidence of such interface phenomena manifested as an apparently autocatalytic action. Thus, in a determination of the dissociation pressure of sodium bicarbonate Lescouer[24] observed that the development of pressure occurs "slowly at first, then more quickly towards the end. . . . It has seemed to me, moreover, that the final equilibrium was obtained more rapidly the more the proportion of dissociated salt increased." Experiments undertaken in the Princeton laboratories

[22] *Jour. Phys. Chem.*, **17**, 567 (1913).
[23] *J. Amer. Chem. Soc.*, **43**, 2017 (1921).
[24] *Ann. Chim. Phys.*, (6), **25**, 430 (1892).

on the dissociation of ammonium meta-vanadate, which yields a colored oxide, thereby facilitating visual control of the nature of the dissociation process, has given qualitative evidence of the interface phenomenon. The ready decomposition of the finely crystalline salt has prevented decisive proof of this possibility.

As regards interaction between a solid and a gas, the case of copper oxide reduction by hydrogen and by carbon monoxide, may now be supplemented by the cases of nickel oxide and vanadium pentoxide. These oxides, when reduced at low temperatures, show the phenomenon of auto-acceleration, and in the latter case the interface is rendered visible by the change from a red-brown to a blue-black oxide. Dr. R. M. Burns reports the same feature in the reduction of vanadium pentoxide in benzene-air mixtures. It is anticipated that this list of oxides could be greatly extended.

Langmuir [25] has pointed out that the hydration of a completely dehydrated substance should show the same auto-acceleration. An observation recently made independently by several workers in the Princeton laboratories seems to verify this conclusion experimentally. The dehydration of ethyl alcohol was undertaken with the aid of lime, which test showed to be "over burnt." For two days the lumps of lime remained intact in the alcohol. On the third day a small amount of powder appeared alongside the lumps of lime. while treatment for an additional twenty-four hours resulted in the complete disintegration of the whole of the lime lumps. Qualitatively, at least, this is in accord with the idea of interface activity.

Now the reactivity conferred on a molecule by reason of the proximity of a molecule of decomposition product can also be secured by admixture of the reacting species with a suitable foreign substance. The conclusions of Hulett and Taylor and of Kendall and Fuchs have already been cited in this regard. Doubtless it is oftentimes this effect which accounts for the enhanced activity of a catalytic agent when admixed with small amounts of a suitable foreign substance. Such admixtures are termed catalyst "promoters" and their utilization in technical catalysis is a growing development of the catalytic art, as the appended table of examples will show. A summary of the principal examples of promoter action has already been compiled by Pease and

[25] *J. Amer. Chem. Soc.*, 387, 2263-2267, (1916).

Taylor.[20] The mechanism of promoter action has received but little study. It is apparent, however, that a suggestive list of

Reaction	Catalyst	Promoters employed or suggested
Contact sulphuric acid process	Burnt pyrites	Oxides of Cu, V, Ur, Cr, Ni, Co, Al, Be, Zr, Zn, Ce, Th and Di
Ammonia oxidation	Oxide of iron	Oxides of Cu, Ca, Bi, Ce, and Cr
	Platinum	Oxides of Pb and Te
Deacon chlorine process	Cuprous chloride	Chlorides of several elements
Removal of sulphur compounds from gases	Iron oxide	Oxides of Cr, Ce and Th
Production of formaldehyde	Various metals	Metallic couples
Oxidation of aniline to aniline black	Copper sulphate or Vanadium chloride	p-diamine or p. amidophenol
Oxidation of naphthalene	Mercuric sulphate	Copper sulphate
$CO + H_2O = CO_2 + H_2$	Iron oxide	Oxides of Cr, Ni, Al, Ce, Th, Zn, Pb, Ur, Na, Cu, Ag and Cu metallic couples
$2CO + H_2$ excess $+ O_2$	Iron oxide	Oxides of Cr, Ce, Th, La and Al
$2CO_2 + H_2$ excess $+ O_2$	Copper oxide	Oxides of Ce, Ag and Mn
Hydrogenation of oils	Reduced nickel	Reduced copper, iron
Ammonia synthesis	Reduced iron	Reduced Mo, W, Co, Ni, Ur. Traces of alkalies

experimental investigations can be put forward on the basis of activity at an interface. It can readily be seen that if added substances increase the lability of decomposable oxides and their

[20] *Journal of Phys. Chem.*, **24**, 241 (1920).

reducibility, the general level of reactivity of the molecule under such circumstances should be consistently greater than that of the single oxide in absence of such added substances.

There is a little evidence that adsorptive effects may be magnified at an interface. The reduction of copper oxide by both hydrogen and carbon monoxide is very pronouncedly retarded by the presence of oxygen in the reducing gas. This is most readily interpreted on the assumption that adsorbed oxygen protects the interface from attack by the reducing gas. The adsorption of oxygen by copper oxide and by copper is, however, known to be small, so that it would be necessary to assume increased adsorptive capacity at an interface to account for the protective action observed. Experimental test of such a view could be best carried out by adsorption measurements with suitable mixtures of materials, one of which is known to function as a promoter to the catalytic activity of the other. In a case recently studied by Taylor and Neville, evidence of enhanced reactivity and of adsorption was obtained by admixture of various substances with carbon, as the subjoined table shows:

Catalyst %	Interaction of C and H_2O at 570°. Gas produced. C.c./min.	Interaction of C and CO_2 at 570°. Gas produced. C.c./min.	Adsorption of CO_2 per g. of C. at 445°. C.c.
20% K_2CO_3	25	2.3	4.4
20 .. Na_2CO_3	7.5	1.0	2.0
7.5 Ni	2.6 (final value)	7.7	1.76
20 .. NaCl	1.8	0.24	0.4
No Catalyst	0.9	0.14	0.33

The interpretation thus far given to these results, however, is that the admixed materials freed the charcoal from mixed oxygen complexes and so increased the active surface of the charcoal for both reaction and adsorption.

Catalyst Poisons.—The inhibiting effect of small quantities of foreign bodies on the activity of a catalyst has yielded satisfactorily to investigation. Poisons may be either permanent or transitory. Thus, silicon compounds, present in the ammonia-air mixture used in the oxidation of ammonia in contact with platinum gauze, are oxidized to silica, are deposited in part on the gauze and destroy its activity by covering up the platinum surface. The poisoning is permanent. Hydrogen sulphide and sulphur compounds transform an iron catalyst in ammonia synthesis and a

nickel catalyst in hydrogenation processes to the corresponding sulphides whose activity is zero. The effect of the sulphur compounds is cumulative and it is necessary to regenerate a catalyst so poisoned by suitable means. In the case of an iron catalyst poisoned by sulphur, it is necessary to oxidize the sulphide and then regenerate the metal by reduction of the oxide. All cases of permanent poisoning require such a renewal of the contact mass before original activity is regained.

Transitory poisons in gas reactions are most generally to be explained on the basis of preferential adsorption of the poison from the gas mixture, even though this latter is present in only minute quantities. Thus, water vapor is a transitory poison in ammonia synthesis in presence of an iron catalyst. It is probable also that water vapor is the real poison in the case of oxygen and carbon monoxide in ammonia synthesis in presence of iron, since both these gases undergo quantitative transformation, to water vapor and to methane and water vapor respectively, under the conditions of the synthetic process. All these poisons are, however, transitory in their action since, after the removal of the harmful constituent, provided the action has not been too prolonged, the original activity of the catalyst is restored. Water vapor is doubtless tenaciously held by reduced iron even at the working temperature of ammonia synthesis, circa 500° C., and when present in only minimal concentrations. It should be noted that a poison may be both transitory or permanent according to the catalyst used. In the case of ammonia synthesis, using uranium carbide (which changes to nitride) as catalyst, water vapor, oxygen, and carbon monoxide are permanent poisons. They convert the nitride to an irreducible uranium oxide, catalytically inert. It is this factor that has militated against the technical use of the otherwise very excellent uranium compound as a catalyst in ammonia synthesis.

Metallic catalysts are occasionally poisoned by other metals. Lead, mercury and zinc are marked catalyst poisons for platinum in a variety of catalytic actions. Mercury vapor is a powerful catalyst poison to copper and nickel as hydrogenation catalysts.

Systematic investigation of the rôle of the poison in the case of palladium and platinum catalysts has been carried out in the last two years by Maxted.[27] The decrease in activity caused

[27] *Journ. Chem. Soc.*, 1920, 117, 1501; 1921, 119, 225; 1921, 119, 1280.

by the poisons, lead, mercury, sulphur, arsenic and zinc, is directly proportional to the concentration of inhibitant from zero concentration up to that producing practically complete inactivity. The occlusive power of palladium for hydrogen varies directly as the amount of sulphur present as inhibitant. The amount of poison (in this case lead) required to reduce the catalytic activity to one-half is very much less than that which reduces the occlusive power to half its original value. This may be explained by the fact that, while occlusion is not confined to the surface, catalysis is a surface phenomenon. With metals showing adsorption without marked occlusion there would doubtless be complete identity between loss of adsorptive power and loss of catalytic activity.

Young's Modulus and Poisson's Ratio for Spruce. H. CARRINGTON. (*Phil. Mag.*, May, 1922.)—The design of aeroplanes has made it necessary to know more definitely the elastic constants of the timber employed. This investigation presents the results of an extensive series of measurements. The smallest value of the modulus is in the direction perpendicular to the length of the tree and tangential to the annual rings. Across the rings the value of the modulus is perhaps 60 per cent. greater than in the first direction, while along the grain of the wood it is about twenty times as great. Determinations of Poisson's Ratio are given for all six possible combinations of linear extension with lateral contraction.

G. F. S.

The following are abstracted from the Annual Report of the Director of the Department of Terrestrial Magnetism, Carnegie Institution of Washington, for 1921. In May, 1921, there occurred simultaneously considerable disturbances of the earth's magnetism, striking displays of the aurora and strong earth-currents. The last named interfered greatly with telegraphy and the aggregate of phenomena has served to direct attention to the relations of the earth to the sun, because at the time there was also great sun-spot activity. "Telegraph companies have requested observers of sun-spot to keep them informed of notable solar phenomena in the hope that they might take whatever advance steps repeated experiences would show practicable for the prevention of serious interruptions from this source in telegraphic transmission. So, likewise, these organizations and interested persons are soliciting information regarding disturbances of the electric currents continually flowing in the Earth's crust.

"The Earth's magnetic changes are being continually recorded at about fifty stations, which, unfortunately, are not distributed over the Earth with the desired uniformity; the great majority are in Europe and only about 20 per cent. are located in the Southern Hemisphere. But matters are still worse as regards earth-currents, since

they are continuously recorded at less than 10 per cent. of the total number of magnetic Observatories."

The non-magnetic vessel *Carnegie* ended its cruise at Washington on November 10, 1921. It and its predecessor, the *Galilee*, have covered a total distance equal to nearly 15 times the circumference of the earth. On land, field work was carried in East Africa and Madagascar and in certain islands in the Pacific. In coöperation with the Government of New Zealand the Department will maintain an observer at the Apia Observatory established by the Germans in 1902. In addition to these activities it is probable that observations are now in progress in Baffin's Land.

Along with the accumulation of data improvement in instruments are made at the Laboratory and the crude material of observation is collated and interpreted with a view to finding an ultimate explanation of the magnetism of the earth.

The United States of America has good reason to be proud of the work done by Dr. L. A. Bauer and by his coadjutors. Not only is the great problem of terrestrial magnetism approaching solution but S. J. Barnett is attacking the underlying cause of general magnetism.

G. F. S.

Tower to Honor Seamen. (*Marine Review*, June, 1922, p. 240.)—A clock and signal tower in the harbor at Montreal has been completed as a memorial to the merchant seamen who lost their lives in the World War. It stands 180 feet above water level at Victoria pier. The clock has four faces, each 12 feet across, and a bell which weighs four tons and is six feet across. The clock will be electrically operated and at noon daily will discharge a bomb of the type in common use on ships. R.

Width of Hard-surface Roads. (*U. S. Department of Agriculture Press Service, Clip Sheet 209.*)—A minimum width of 18 feet for hard-surface roads is recommended by the Bureau of Public Roads. The maximum width of truck body generally permitted is 8 feet, and 5½ feet is the ordinary clearance width of automobiles. At an average speed of 30 miles an hour it is unreasonable to expect the driver of an automobile to drive with the wheels closer than 1½ feet to the edge of the pavement, says the Bureau. For trucks at an average speed of 15 miles an hour, this distance should not be less than 1¾ feet on account of the great width of the rear wheel. Three feet seems to be a minimum safe clearance between bodies. Inasmuch as a certain amount of truck traffic is to be expected on all main country roads, the minimum width of surface should be 18 feet to provide these clearances when an automobile meets a truck.

Where the frequency with which trucks pass each other becomes a big factor, as in the neighborhood of large cities, the minimum width of pavement should be 20 feet to provide a clearance of 3½ feet and a safe distance of wheels from edge of pavement. R.

PHYSICS OF THE THREE-ELECTRODE BULB.*

BY

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INTRODUCTION.

PROBABLY the discovery and use of the three-electrode bulb mark the most important development in the art of wireless communication for, as sender or receiver, it is the "working" part of modern wireless sets. Its invention followed Edison's discovery of the "Edison" or "thermionic" effect, its study by Elster and Geitel, 1882–1890, and by Fleming, 1890–1896, and the development of the theory of the effect by Richardson since 1904. It is interesting to note, in passing, that the thermionic effect was discovered and studied by physicists of the seventeenth century, but the subject was dropped before significant results were obtained—to be revived and put to important use 200 years later.

The Edison effect can easily be demonstrated by wrapping tin-foil around the glass of an incandescent light bulb—taking care not to make contact with the screw base—and connecting a galvanometer in series with a battery between the tin-foil and one of the wires feeding the filament. If the battery is connected so as to make the tin-foil *negative* with respect to the filament, no deflection of the galvanometer is observed. If, however, the tin-foil is *positive*, the galvanometer indicates a current. This current comes as a stream of negative electrons from the hot filament, through the glass to the tin-foil, through the galvanometer and battery and back to the filament. No current flows in the above circuit until the glass inside the tin-foil becomes hot enough to be sufficiently conducting. This experiment may be performed with a tungsten filament lamp, but an old style carbon filament lamp gives a larger current unless the tungsten lamp is run over-voltage.

NATURE OF THERMIONIC EMISSION.

The principal investigations of the emission of electrons from

* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute, held Thursday, April 13, 1922.

hot bodies have dealt with the effects of the nature of the metal and its temperature on the number of electrons emitted per second and on the velocities with which they are emitted.

It is found that the electrons emitted from any pure metal at a given temperature emerge from it with all possible velocities between zero and a very high value, probably infinity, and that the relative numbers with various velocities are distributed according to Maxwell's probability law, with an average velocity which is proportional to the absolute temperature of the metal. In other

TABLE I.

Energy of Emission less than	at 1050° K. (volts)	at 3150° K. (volts)	Fraction
$\bar{V}$	0.27	0.80	0.392
$2\,\bar{V}$	0.54	1.60	0.112
$3\,\bar{V}$	0.80	2.40	0.032
$4\,\bar{V}$	1.07	3.20	0.0086
$5\,\bar{V}$	1.34	4.00	0.0019
$6\,\bar{V}$	1.60	4.80	0.00042
$7\,\bar{V}$	1.87	5.60	0.00011
$8\,\bar{V}$	2.14	6.40	0.000027
$9\,\bar{V}$	2.40	7.20	0.0000060
$10\,\bar{V}$	2.67	8.00	0.0000014

words, the relative numbers with different velocities are the same as if the electrons were molecules of an ideal gas. It was first thought [1] that these velocities were the same as if the electrons were molecules of an ideal gas *at the temperature of the emitting metal,* but recent investigation has shown that their average kinetic energy is about twice this large, as if characteristic of about *twice the temperature of the metal.* An idea of the distribution of velocities among the emitted electrons may be gained from Table I, in which the velocities are expressed in terms of the equivalent number of volts V from the relation $\frac{1}{2} m v^2 = \frac{eV}{300}$.[2] The last column gives the fraction of all emitted electrons whose velocities

[1] Richardson and Brown, *Phil. Mag.,* 93, 1908; Richardson, "Emission of Electricity from Hot Bodies," Chap. V.

[2] e and m are the charge and mass of an electron and 300 is a factor to convert from electrostatic units of potential to volts. V is the number of volts of potential drop in which an electron would acquire a velocity v. $\bar{V}$ is the average energy, in volts.

exceed the value indicated in the other columns. For instance, at 1050° absolute, 0.0019 of the emitted electrons have energies exceeding five times the average energy, or possess sufficient kinetic energy to pass against a retarding field of 1.34 volts.

This type of velocity distribution is similar to that among the molecules of a vapor which have just escaped by evaporation from a liquid surface. It suggests that thermionic emission is really an evaporation of electrons from the surface of the hot metal.

Richardson first applied this conception to the theory of thermionic emission. Within the metal there are electrons with velocities distributed as if they are molecules of an ideal gas. Those which strike the surface will escape if their kinetic energy exceeds the work which they must do against the retaining forces at the surface. These retaining forces include the attraction exerted on the escaping electron by the positive charge induced by it on the surface, and the total work done against these forces is the "heat of evaporation" of the electrons. This work is often called the "work function" and written as $e\phi$, where ϕ is the equivalent potential difference. On this theory, Richardson showed that the thermionic current per square centimetre of emitting surface should be

$$i = N e \sqrt{\frac{k}{2\pi m}} T^{\frac{1}{2}} \epsilon^{-\frac{e\phi}{kT}}, \qquad (1)$$

where N is the number of free electrons per unit volume in the metal, k is the Boltzmann gas constant in $pv = nkT$, and T is the absolute temperature.

The same theory, applied to the Thomson effect in metals, indicates that N is closely proportional to $T^{\frac{1}{2}}$ so that the true variation of thermionic current with temperature should be given by the equation

$$i = A T^2 \epsilon^{-\frac{e\phi}{kT}}, \qquad (2)$$

in which A is a constant. The same equation was derived by Richardson on more general grounds, without postulating the existence of free electrons within the metal, and Dushman [3] has recently given grounds for supposing that A has the same value for all metals, and has calculated its value. Thus

[3] Paper at Washington Meeting of American Physical Society, April, 1922.

the thermionic properties of metals seem to be determined entirely by the temperature T and the work function, or "latent heat of evaporation of an electron," ϕ. To obtain large thermionic currents it is necessary to use a substance with a small value of ϕ and with a high enough melting point to permit its use at a high temperature.

Equation 2 has been tested over an enormous range, with sufficient temperature variation to produce a variation of ten million million fold, or 10^{13} fold, in the thermionic current, without detecting any inaccuracy in equation 2.[4] Table II gives some actual

TABLE II.

Temperature	Thermionic Current	
1050°K.	0.000000235	microamps.
1200	0.000169	per sq. cm.
1350	0.0282	
1500	1.70	
1650	49.0	
1800	809.	
1950	8730.	
2100	67000.	
2250	394000.	etc.

currents from a tungsten wire. Currents as large as 8 amperes per square centimetre of emitting surface have been obtained. A convenient method of testing equation 2 is illustrated by Fig. 1, in which the equation is plotted in its logarithmic form. In this form, the graph of the observed values of i and T should give a straight line, such as BC.

THE "WORK FUNCTION" ϕ.

The slope of the curve, as plotted in Fig. 1, gives the value of the work function ϕ characteristic of the metal from which the plotted values were obtained. This value, and the intercept $\overline{OA}$, determine the other constant A.

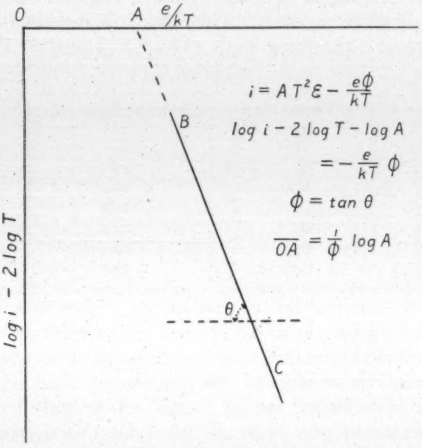
Since the work function ϕ is of the nature of a heat of evaporation, we should expect a metal to be cooled by its thermionic emission just as a liquid is cooled by evaporation. This was found by Cooke and Richardson [5] to be the case. They used a metal fila-

[4] K. K. Smith, *Phil. Mag.*, 1915.

[5] *Phil. Mag.*, **20**, p. 173, 1910; **25**, p. 624, 1913.

ment as one arm of a sensitive Wheatstone's bridge, which provided its heating current and measured its resistance. The filament was surrounded by a coaxial electrode which could be charged negatively or positively with respect to the filament so as to prevent or permit the emission of a thermionic current from the filament. When this emission was permitted, the temperature

FIG. 1.



of the filament was observed to decrease. From the additional amount of energy of heating current required to bring the filament back to its original temperature, the total rate of loss of heat by evaporation of electrons was determined. From this the heat of evaporation per electron, ϕ, was calculated and found to agree with the value obtained as in Fig. 1.

A third method of measuring ϕ is to consider it as a "heat of condensation." That is, heat should be developed in a metal when electrons pass into it through its surface. This was also proved and ϕ measured by Richardson and Cooke,[6] who observed the increase in temperature of a thin metal strip, which formed one arm of a Wheatstone's bridge, when electrons passed into it from a neighboring hot filament.

[6] *Phil. Mag.*, **20**, p. 173, 1910; **21**, p. 404, 1911.

Finally, there is a relation between the values of ϕ and the contact difference of potential of metals which is useful in estimating or predicting values of ϕ for metals which have not been accurately investigated by the preceding methods. Consider two metals (1) and (2), connected at the junction J and placed in an enclosure at constant temperature. Calculate the work done in the processes involved in taking an electron around a cycle as follows: Starting in (1), take it out through the surface of the metal, doing work $e\phi_1$ on it. Then take it to a point just outside the surface of (2), doing work $e(V_2 - V_1)$ against the contact

TABLE III.

Metal	ϕ (in volts)
Pt	5.3
W	4.4
Mo	4.04
Ca	3.04
Na	2.65
BaO	3.65
CaO	3.48

difference of potential between the metals. Then take it through the surface into (2), in which process it does work $e\phi_2$. Finally, take it around through the metals, across the junction J to the starting point, doing work at the junction equal to eP, where P is the Peltier coefficient for the metals. The work done against metallic resistance may be neglected, since this depends on the square of the current and we may imagine the process to be performed as slowly as we please. The total work done must be zero, since it is a reversible cycle at constant temperature. Therefore,

$$V_1 - V_2 = \phi_1 - \phi_2 + P. \qquad (3)$$

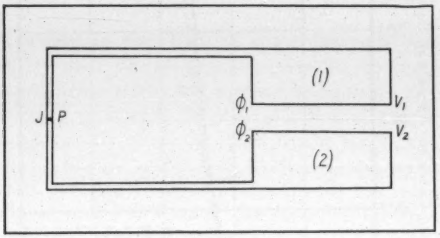
P is so small as to be practically negligible, whence we see that the difference between the work functions of two metals equals their contact difference of potential. A very electropositive metal has a small value of ϕ. Equation 3 has been verified by direct experiment with only moderate accuracy, since the values of V are very difficult to determine free from spurious effects. Indirect verification of the equation has, however, been quite convincing.

Table III gives a few typical values of ϕ. Expressed in equivalent volts, the average kinetic energy of a gas molecule is 0.13 volt at 1000° K., 1.3 volts at 10,000° K., and 6.5 volts at

50,000° K. We see that ordinary temperatures are sufficiently low to keep electrons from rushing freely out of metals, only a minute fraction of them having sufficient energy to escape.

It is desirable, in a three-electrode bulb, that the thermionic emission from the filament be large, homogeneous as regards velocity distribution, obtained with a minimum expenditure of battery power, and absolutely constant under constant external conditions. Large currents are obtained with large area of emitting surface, high temperature and small ϕ. Tungsten is there-

FIG. 2.



$$V_1 - V_2 = \phi_1 - \phi_2 + P$$

fore superior to platinum, for it combines a smaller value of ϕ with a much higher melting point. Homogeneity of velocities demands low temperatures, which, in turn, necessitate a substance with a small value of ϕ. For this reason, platinum strips coated with the oxides of the electropositive and fairly non-volatile alkaline earths are advantageous. These are also advantageous because of their operation with minimum expenditure of battery power, since they give good emission at a dull red heat, whereas tungsten must be heated to bright incandescence. Pure metals are probably preferable to oxide coated filaments as regards constancy, although the constancy of the present commercial bulbs with oxide-coated filaments is remarkable.

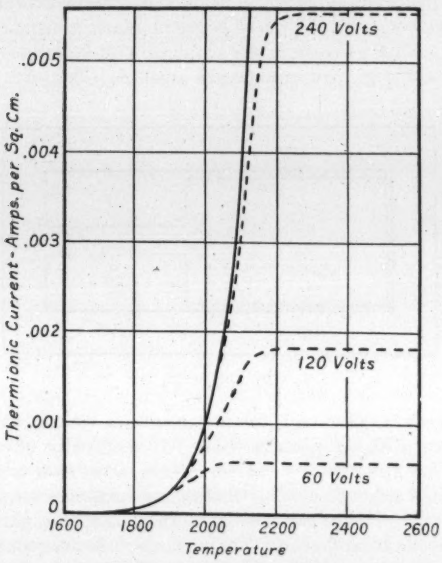
A very recent development which may be important was reported by Langmuir.[7] Thoriated tungsten filaments, given proper heat treatment, become coated with a surface layer of thorium which is very stable unless the temperature is excessive. The filament then has the properties of a thorium filament and com-

[7] *Proc. Am. Phys. Soc.*, Washington meeting, April, 1922.

bines very advantageously a relatively low value of ϕ with ability to operate at a moderately high temperature.

If the prime requirement is a maximum emission, nothing equal to tungsten is known.

FIG. 3.



EFFECT OF SPACE CHARGE.

Although equation 2 gives the total rate of emission of electricity from a metallic surface, the actual thermionic current is often less than this because some of the emitted electrons return to the emitting metal, being forced back by the repulsion of other electrons which have been emitted just ahead of them. The region surrounding the emitting metal contains electrons and thus has a "space charge" which tends to prevent the emission of additional electrons. On the other hand, an electric field may be applied to aid the escape of emitted electrons. The current, therefore, adjusts itself to such a value that the accelerating effect of the applied

electric field is just balanced by the retarding effect of the space charge, so that the resulting electric field just outside the surface of the metal is zero.

Actually, due to their initial velocities, electrons will be able to escape against a small opposing field, so that the current is really a little larger than that which would just give the balance suggested above. The emitting surface is surrounded by a region of opposing field which reaches zero at a surface of minimum potential at some point outside the metal. Here the field changes direction and is an accelerating field in the remaining interval to the anode.

Fig. 3 illustrates the effect of space charge in limiting the thermionic current. The heavy curve gives the maximum current possible at each temperature and agrees with equation 2. To obtain such currents, a sufficiently large accelerating electric field must be used to completely offset the effect of the space charge. The effect of using smaller accelerating fields is shown by the broken curves, which give experimental results for 60, 120 and 240 volts, respectively. For a low voltage, the experimental curve departs from the theoretical curve at small currents, whereas the curves at higher voltages agree with the theoretical curve to much larger currents. It is seen that, for 60 volts, the maximum possible current is given at 2050° K., and further increase in the temperature of the filament does not increase the current. Similar maximum currents are characteristic of each other voltage.

For a hot filament, the actual current is seen to depend on the applied voltage, as long as the current is less than that given by equation 2. These currents I_{60}, I_{120}, etc., are found to be proportional to the 3/2 power of the corresponding voltages. Langmuir has shown [8] that the above considerations lead to a relation between the current density i and the voltage V, for values of i considerably less than those given by equation 2, of the form

$$i = 2.33\ (10)^{-6}\ d^{-2}\ V^{3/2} \text{ amps. per sq. cm.} \qquad (4)$$

if the electrodes are parallel plates distant d apart, and

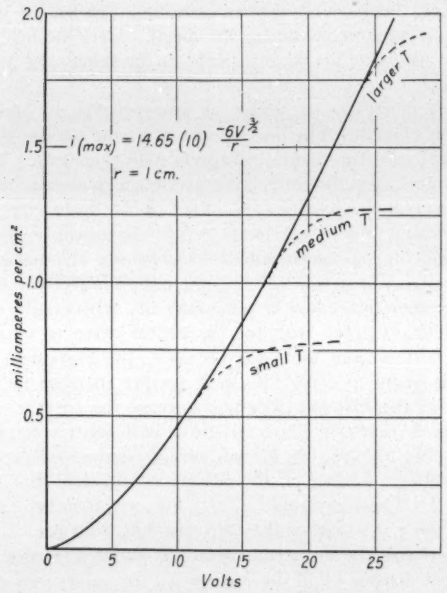
$$i = 14.65\ (10)^{-6}\ r^{-1}\ V^{3/2} \text{ amps. per sq. cm.} \qquad (5)$$

for a small straight filament surrounded by a coaxial cylinder of radius r.

[8] *Phys. Rev.*, **2**, p. 450, 1913.

The actual relation between filament current and voltage is shown by Fig. 4, which was calculated for the case of a cylindrical anode of unit radius. The solid curve represents equation 5. At any temperature the currents depart from this curve as the saturation value given for that temperature by equation 2 is approached.

FIG. 4.



Note that for 20 volts, for instance, it is impossible to obtain a current greater than 1.3 m.a., no difference how hot the filament is. But a greater current could be obtained at 20 volts and high temperatures if the distance r between the electrodes were diminished (or, as we shall see later, if positive gas ions are present to neutralize the negative space charge. The above conclusions regarding the effect of space charge apply only to the case of electrodes in a high vacuum).

ELECTRON ATMOSPHERES.

Let me now call attention to a necessary consequence of the facts of thermionic emission, *i.e.*, to the existence of an electron atmosphere at the surface of every metal and extending out with diminishing density to greater distances from its surface. We may picture to ourselves the cause of this atmosphere in the following way. Electrons within the metal continually reach its surface with sufficient kinetic energy to carry them a greater or less distance out, against the attractive forces (which give rise to the work function) which tend to draw them back into the metal. Some few have sufficient energy to escape. The rest are drawn back into the metal, after a short-lived freedom. Thus, at any given distance from the surface, there is a certain average number of electrons per unit volume, or electron density, which remains constant although the particular electrons in this group are continually changing. At higher temperatures this electron atmosphere is denser and extends farther from the surface, owing to the greater kinetic energy of the electrons. Electrons in this atmosphere will collide with each other and behave as molecules of a gas in a field of force.

This force of attraction back toward the metal may arise jointly from several causes, but, unless the atmosphere is very dense, the principal cause is probably the attraction due to the equal positive charge induced by each escaping electron on the surface of the metal. If we assume, as a first approximation, that this is the *only* cause, and that the surface of the metal may be considered as perfectly continuous, instead of being composed of discrete atoms with intervening gaps, we may draw conclusions regarding the electron atmosphere as follows:

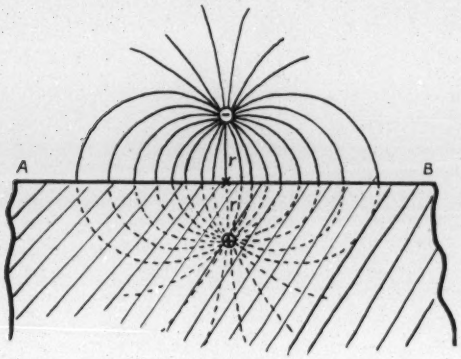
Let AB be the surface of the metal and an electron be distant r from it. The electric field due to the induced positive charge on the surface is the same as if due to the positive "mirror image" of the electron at a depth r within the metal. The force of attraction of the electron toward the surface is, therefore $F = e^2/4r^2$. The work done by an electron which escapes from the surface is thus

$$W = e\phi = \int_a^\infty \frac{e^2}{4r^2}\, dr = \frac{e^2}{4a}, \qquad (6)$$

where a is the distance from which the electron started, so that $2a$ is the initial distance between the electron and its accompanying positive charge.

According to a well-known theorem of statistical mechanics, the numbers of electrons n_1 and n_2 at any two different positions

FIG. 5.



in a field of force depends on the work ${}_2W_1$ required to take an electron from the second to the first position according to the equation

$$\frac{n_1}{n_2} = \epsilon^{-\frac{{}_2W_1}{kT}} \tag{7}$$

where ϵ is the base of the Naperian logarithms and T is the absolute temperature. If the second position is the initial position at a distance a, so that $n_2 = n_a$, and if the first position is any position distant r, we have the number of electrons per unit volume at distance r given by equations 7 and 6 as

$$n = n_a \epsilon^{\frac{e^2}{4kT}\left(\frac{1}{r}-\frac{1}{a}\right)}. \tag{8}$$

To determine n_a we notice that the saturation value of the thermionic current, as given by equation 2, must depend on the den-

sity n_∞ at relatively great distances $r = \infty$ from the metal in a way which is easily shown by kinetic theory to be

$$i_{\max.} = n_\infty e \sqrt{\frac{kT}{2\pi m}} \quad . \qquad (9)$$

This gives the value of n for $r = \infty$, and hence enables the constant n_a in equation 8 to be determined.

From these equations, I have calculated the electron densities given in Table IV at various distances from the surface for the case of tungsten, $\phi = 4.4$ volts and $i_{\max.} = 8$ amperes per square centimetre at 3000° K., whence $2a = 1.6(10)^{-8}$ cm.

TABLE IV.

d (cm.)	n (300°K.)	n (1000°K.)	n (3000°K.)
$0.8\ (10)^{-8}$	$3.0\ (10)^{20}$	$3.0\ (10)^{20}$	$3.0\ (10)^{20}$
$1.0\ (10)^{-8}$	$1.5\ (10)^{5}$	$7.6\ (10)^{15}$	$8.7\ (10)^{18}$
$2.0\ (10)^{-8}$	$1.9\ (10)^{-28}$	$4.3\ (10)^{6}$	$7.1\ (10)^{15}$
$4.0\ (10)^{-8}$	$7.4\ (10)^{-42}$	$1.0\ (10)^{2}$	$2.1\ (10)^{14}$
$1.0\ (10)^{-7}$	$4.4\ (10)^{-51}$	$2.0\ (10)^{-1}$	$2.5\ (10)^{13}$
$1.0\ (10)^{-6}$	$1.0\ (10)^{-58}$	$3.6\ (10)^{-3}$	$6.8\ (10)^{12}$
∞	$3.0\ (10)^{-67}$	$3.0\ (10)^{-3}$	$5.9\ (10)^{12}$

Evidently the electron atmosphere is extremely rare at appreciable distances from metals at ordinary temperatures. Experimental evidence regarding its detection at ordinary temperatures is conflicting. R. W. Wood[9] reports currents of several milliamperes between optically flat plates of speculum metal, separated by fine quartz fibres, with application of only a few millivolts. On the other hand, Millikan and Shackelford were unable to draw electrons out of gas-free metals with potential gradients lower than about four million volts per centimetre, and suggest that such electron discharges previously reported are due, in some way, to surface impurities.[10] However this may be, the fact of thermionic emission proves the existence of such atmospheres at higher temperatures, and there is no reason for doubting their existence at lower temperatures, although with lower density and extending not so far from the surface.

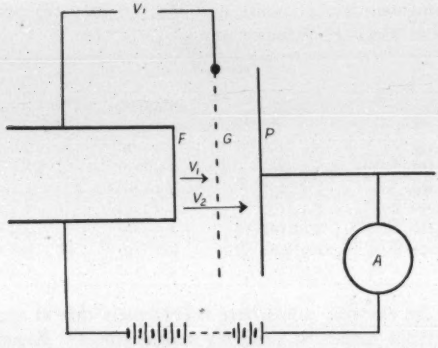
Recently, in our laboratory, a significant proof of electron

[9] *Phil. Mag.*, **24**, 1912.

[10] *Phys. Rev.*, **15**, 1920.

atmospheres at high temperatures was obtained. An incandescent tungsten wire was mounted close and parallel to a tungsten strip. The thermal expansion of the leads caused the wire slowly to approach the strip. The ammeter, in series with a battery and the gap between wire and strip, registered the normal thermionic current until the approach was very close, when the current began rapidly to increase with increasing proximity. Before actual contact was made, the thermionic current had risen to many times

FIG. 6.



its normal value. This must have been due to an approach within the region in which the electron atmosphere around the filament showed a noticeable increase in density.

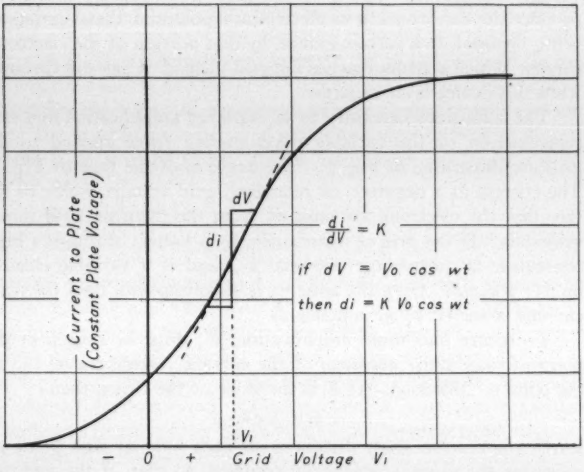
It should be emphasized that the above calculation of densities is necessarily very rough. Actually the metal surface consists of discrete atoms, so that the law of force is more complicated than that underlying equation 6. Furthermore, the effect of the space charge will modify the force on an electron at any point, tending to spread the electron atmosphere to a greater distance from the metal, but with less density near the metal. Nevertheless it is probable that for points not too near the surface, the electron densities are somewhat as given in Table III.

ELECTRIC VALVES.

An electric valve is a device which permits the passage of an electric current in one direction only. It is evident that any

combination of two neighboring conductors not in contact, one of which is surrounded by an electron atmosphere, whereas the other is not, constitutes an electric valve. Electrons can pass continually from the one with the atmosphere to the other, but cannot pass in the reverse direction. Now a hot and a cold metal constitute such a combination. The hotter is the hot metal, the greater is

FIG. 7.



the current-carrying capacity of the valve; while the colder is the cold metal, the more perfect is the rectification. The "Kenetron" is an example of this type of thermionic rectifier. I have wondered if the action of crystal rectifiers may not be due to some peculiarity of distribution of electron atmospheres around the surfaces of crystals.

THE THREE-ELECTRODE VALVE.

Fig. 6 shows the elements of a three-electrode valve, and their simplest mode of connection. Electrons are emitted thermionically by the filament F and pass toward the perforated grid G if the field V_1 is in the appropriate direction. Since the grid has very large mesh, most of the electrons which reach it pass through the

openings and are attracted to the plate P. The ammeter A, or a telephone receiver or other detecting device, is operated by this plate current.

If V_1 is connected to a source of variable electromotive force, the field V_1 varies and consequently the current reaching and passing through the grid will vary. If the thermionic current is large, these variations in the plate current may be very large, even though the current applied to the grid is only large enough to produce the variations in its electrostatic potential, these variations being opposed, to a certain extent, by that portion of the electronic current, which actually reaches the grid instead of passing through. Thus this device is an *amplifier*.

The conditions necessary to secure large amplification and true reproduction of the variable electromotive force applied to the grid are illustrated in Fig. 7. The curve is of the type of Fig. 4. The current at a negative, or retarding, grid voltage is due to the fact that the electrons are emitted from the filament with initial velocities. If the grid is maintained, by a battery through a high resistance, at an average potential V_1, and if a variable electromotive force dV from the antenna is superimposed, then the plate current is varied by an amount di.

To secure maximum amplification, V_1 must be chosen at the point of maximum steepness of the current-voltage curve, *i.e.*, at the point of inflection. If K is the slope of the curve, then

$$di = K\,dV. \tag{10}$$

Furthermore, for short distances on each side of this point of inflection the slope is practically constant, so that, if the variable e.m.f. to the grid is a simple harmonic function of the time,

$$d\,V = Vo \cos w\,T\,,$$

then (11)

$$d\,i = K\,Vo \cos w\,T\,.$$

Thus the amplified current faithfully reproduces the current which is being amplified. If two-stage amplification is desired, the amplified current from the first-stage tube may be passed through the primary of a step-up transformer, whose secondary is connected to the grid of the second-stage tube.

GAS-FILLED TUBES. DETECTORS.

The preceding relations between voltage and thermionic current hold true only when the electrodes are in so good a vacuum

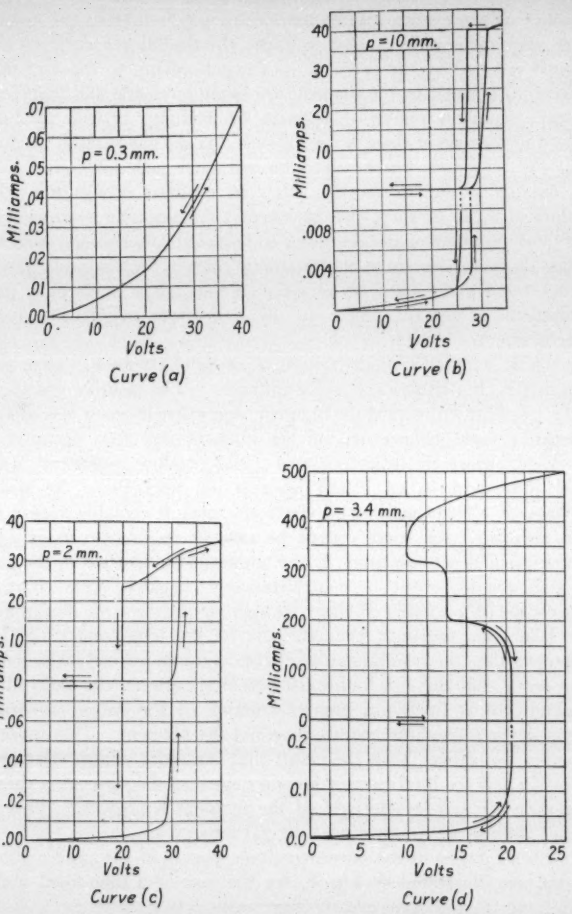
that effects of collisions of electrons with gas molecules are negligible. When even a minute amount of gas is present the results are very different. At low voltages the thermionic currents are much reduced by the presence of the gas, owing to the fact that electrons emitted by the filament are likely to collide and therefore escape from the region of negative space charge around the tube less quickly than if the gas were absent. If the gas is multi-atomic, the electrons start practically from rest after each collision, while, if the gas is monatomic, the electrons rebound elastically. The effect of a gas is, therefore, to increase the negative space charge around the filament and therefore to reduce the thermionic current. This decrease is greater in monatomic than in multi-atomic gases, since the zig-zag path of an electron through a monatomic gas causes it to remain longer in the immediate neighborhood of the filament.

If the voltage is high enough to cause electrons to ionize gas molecules, the situation is quite different. The positive gas ions, which are drawn toward the filament, neutralize more or less of the negative space charge around the filament and thus permit the escape of more electrons, some of which produce additional positive ions, and so on. Each positive ion neutralizes the space charge of a large number of electrons, since it remains longer in the region of the space charge because of its greater mass and consequent slower motion. If the amount of ionization in the gas is sufficient to permit, by neutralization of negative space charge, the escape of a number of electrons approaching that for maximum or saturation emission characteristic of the temperature of the filament, then the resultant space charge becomes less negative, with the result that the distribution of potential between the electrodes changes so as to give a greater fraction of the entire potential drop in the immediate neighborhood of the filament. This favors further ionization, with the result that the space charge becomes positive and the total current becomes equal to the saturation thermionic current characteristic of the filament temperature, plus a small additional current due to the gas ions.

These stages in the current-voltage curve, in the presence of a gas, are illustrated by Fig. 8, for the case of a tube filled with helium at the indicated pressures.

Curve (a) is at a pressure and thermionic current density too low to give an arc. Indication of ionization is given by a "break" in the curve at 20 volts. Curve (b) shows an arc pro-

FIG. 8.

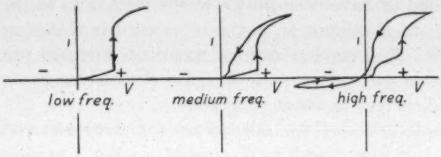


duced by emission from a relatively cool filament. Not sufficient ionization to produce the arc was obtained until a voltage of

28 volts was applied. With decreasing voltage, however, the arc was maintained at a lower voltage. Curve (c) is a case of a hotter filament, where the arc still strikes at a voltage higher than 20 but breaks definitely at this voltage. With the hottest filaments, the arc both strikes and breaks at the definite minimum of 20 volts, although it may be maintained at a lower voltage, curve (d).

The relative increase in current when the arc strikes may be enormous, amounting to as much as 50,000 fold with scarcely noticeable change in voltage at 20 volts. A two- or three-electrode tube could therefore be used as a *detector* of very great sensitive-

FIG. 9.



ness by adjusting the voltage to a value just less than the striking voltage, so that the increased voltage impressed by the incoming signal causes the arc to strike. Almost infinite amplification may be thus secured. Even if the arc is not used, the gas pressure or filament temperature being too low to produce it, very great amplification may be obtained because of the steepness of the current voltage curve beyond the ionizing point.

Unfortunately, however, the use of ionized gases to increase amplification is attended with complications which probably render such methods of little value except for very special work. Chief among these difficulties are non-reversibility and lag effects, which produce serious distortion. Fig. 8 illustrates that, except under special conditions, the course of the current-voltage curve depends upon whether the voltage is increasing or decreasing. This is due to a difference in the distribution of potential in the space between the electrodes in the two cases.

Lag effects, as illustrated in Fig. 9, are due to the time required for the recombination of ions and for abnormal, or partially ionized, molecules to return to their normal stable conditions. These curves are approximate reproductions of some very interesting unpublished results obtained by Mr. Kannenstine, at the

University of Chicago. They represent oscillograph records of the variation of the current, due to thermionic emission from a filament in an atmosphere of helium gas, as the voltage between the electrodes is varied. Curve (a) represents a stage intermediate between curves (a) and (b), Fig. 8, when the voltage is varied slowly. Curve (b) is taken under similar conditions with the voltage varied more rapidly, as by a 60-cycle e.m.f. Curve (c) shows the results with an e.m.f. of still higher frequency. In curve (b) on the return curve, some of the helium molecules have persisted in an abnormal state which renders them ionizable at voltages down to about four volts. In curve (c) this effect is more pronounced, since the time is shorter. Not all the ions have recombined or have been drawn to the electrodes in the period of the cycle, as is evident from the reverse current during the negative cycle. And some abnormal molecules are still present when the positive part of the cycle is again reached as is shown by the increased current at about four volts.

Consideration of the operation of a three-electrode bulb, as presented in Fig. 7 and its discussion, makes it evident that gas-filled bulbs with characteristics, as shown in Figs. 8 and 9, will not function satisfactorily as amplifiers for ordinary high-frequency transmission. As detectors, valves, keys, etc., they may be of considerable advantage.

CONCLUSION.

It is evident to you that I have kept closely to my subject, The *Physics* of the Three-electrode Bulb, and have attempted to give a survey, necessarily incomplete, of some of the physical phenomena which have become of great practical importance in their applications and which have also had very important bearing on our ideas regarding the nature and structure of matter and electricity. I have not attempted to discuss details of practical operation of three-electrode bulbs, for two sufficient reasons: Time did not permit discussion of both aspects of the subject, and I am not a practical expert in the use of three-electrode bulbs.

For any who are interested in practical uses of the three-electrode bulb, the following books are suggested: "Radio-Communication," Mills; "Thermionic Vacuum Tube and its Applications," Van der Bijl; "Vacuum Tubes in Wireless Communication," Bucher.

A PRECISION HIGH-SPEED OSCILLOGRAPH CAMERA.*

THE PRECISE MEASUREMENT OF SMALL TIME INTERVALS

BY

E. A. ECKHARDT, Ph. D.

Physicist, Chief of Sound Laboratory, National Bureau of Standards.

In the oscillographs generally used in the electrical laboratories of the United States, the more or less sinusoidal wave of the 60-cycle supply is ordinarily used to provide the time scale. This is generally adequate in investigations involving the frequencies of ordinary power supply. On the other hand, the oscillographic study of the phenomena attending (1) the closing or opening of circuits, (2) fuse protector or circuit-breaker action, (3) dielectric break-down, (4) relay and transformer action, often require a more precise time scale.

A further requirement of many of these problems is an increased film speed. This is necessary to draw out the record so that the details of the recorded event shall not be confused by too close crowding, or in order to obtain the required accuracy of time measurement.

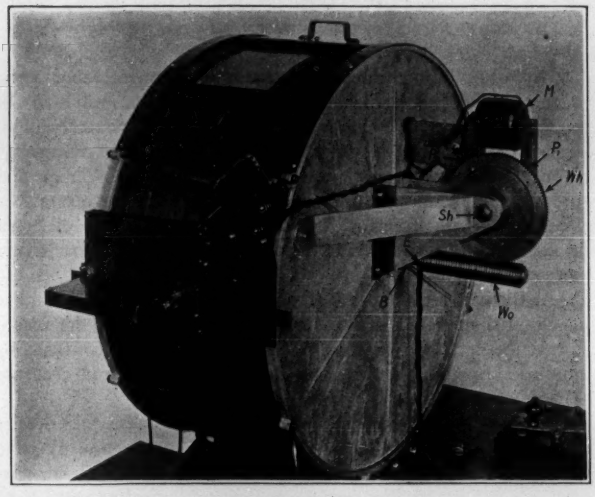
Problems demanding the use of high film speeds and precise time scales have led to the development in our laboratory of a high-speed oscillograph camera, and associated time-scale apparatus which have proven very convenient and effective as tools of research and of measurement and consequently their description here seems worth while.

The character of our laboratory activity made it seem advisable not to design the high-speed camera as an integral part of any one oscillograph, but rather as a complete camera unit with sufficient flexibility to make it available for use with any one of a number of oscillograph types. The variety of combinations in which the camera has already been used has fully justified this feature of the design.

* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute held Thursday, December 8, 1921.

If long films are to be used one has the choice of unrolling the film from one small drum on to another during the exposure interval, or of using a single drum of sufficiently large circumference to accommodate the entire length of film. The first alternative involves the starting in motion of the film as the exposure begins. This makes uniform film-speed quite difficult to attain. The

FIG. 1.



The high-speed oscillograph camera.

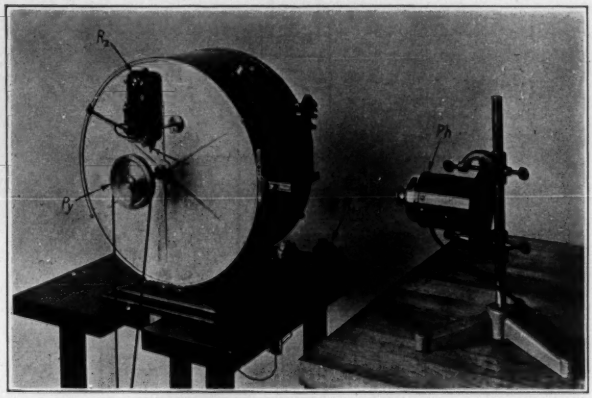
large drum, on the other hand, can be brought up to speed prior to the exposure. Conditions are, therefore, favorable for uniform motion of the film at high speeds. The shutter mechanism, however, in this case must operate with precision, so as to avoid double exposure on any portion of the film.

THE CAMERA.

The drum of our high-speed oscillograph camera is approximately five feet in circumference and four inches wide. It is mounted on a shaft, both ends of which protrude from a light-

tight housing which in all dimensions, save its width, is just large enough to accommodate the drum without interference. The width of the housing is somewhat over eight inches, so that drum and shaft can be moved axially within it for a distance equal to the width of the drum. The film stretched over the periphery of the drum presents a cylindrical surface. By giving to the drum an

FIG. 2.



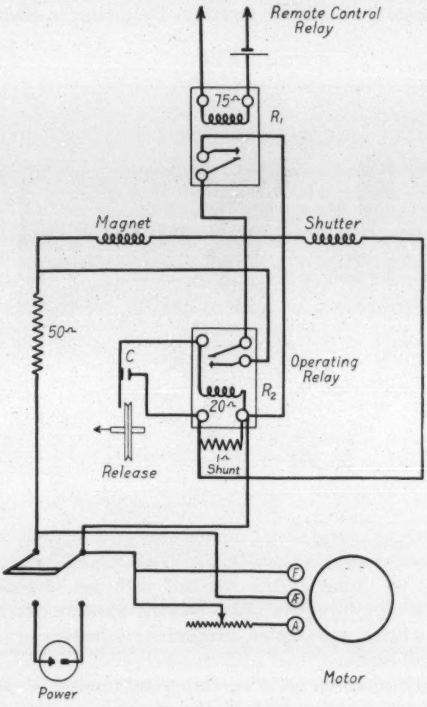
The camera set up to obtain oscillogram of loud-speaking telephone diaphragm motion.

axial as well as a rotational motion, the oscillograph record is traced on the film as a spiral band, similar to a screw thread. By moving the drum axially one-half inch per revolution and exposing the film through a width-limiting aperture one-half inch wide, placed before the shutter, a record forty feet long is obtained on a five-foot film.

The mechanism for securing this spiral motion is simple and positive in action. One end of the protruding shaft carries a phosphor-bronze worm *Wo* (see Fig. 1), the inner edge *E* of which rests against the bearing bushing *B* when the drum occupies its idling position in the housing. The driving pulley *Py* is on the other end of the shaft, as shown in Fig. 2. Except during exposure the cast-iron wheel *Wh* (see Fig. 1) idles on its shaft *Sh*, being driven by the worm *Wo*. The energizing of the magnet

coil M causes the pole pieces P_1 and P_2 of the electromagnet to grip the cast-iron wheel, the idling motion of which is instantly arrested. The worm then necessarily feeds out along the wheel,

FIG. 3.



Wiring diagram of camera.

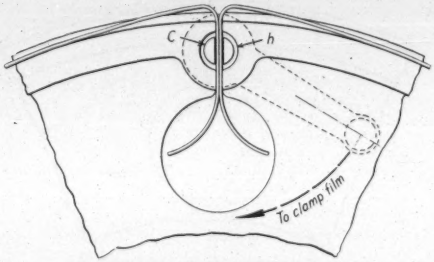
thus imparting to the drum the desired axial motion. The cameras in our laboratory are equipped with readily interchangeable worm and wheel combinations, so that axial motions of either one-fourth or one-half inch per revolution may be had, corresponding respectively to sixteen and eight revolutions for a complete exposure.

OPERATION OF THE CAMERA.

Ordinarily it is found convenient to use the camera in a dark room, as then the loading operation simply involves the turning off of the lights (with the exception perhaps of the safe light), the opening of the housing, the putting of the film in place, and the closing of the housing. The camera is then ready for use, and the lights may be turned on until the exposed film is to be removed for development.

If the work for which the camera is to be used is being prosecuted in a room the darkening of which is not feasible, preparation must be made for rolling the entire camera into the dark room, or else some sort of daylight-loading device must be provided.

FIG. 4.

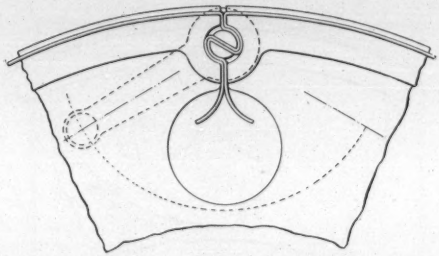


Film clamping device. Film ready to clamp.

With the loaded camera in position before the oscillograph the drum is brought to the desired speed. The exposure is begun by operating the relay R_2. Its operation energizes the wheel-gripping and shutter-opening electromagnets simultaneously, since their windings are connected in series. The exposure and the axial motion of the drum, therefore, begin simultaneously. After the drum has moved axially any predetermined distance, which may be all or only part of that available, the driving pulley Py whips open a contact C. The opening of this contact operates to restore the short-circuit across the two electromagnets. The closing of the shutter and the ceasing of the axial motion follow, again simultaneously. The power switch is then opened and the drum permitted to come to rest, whereupon the film may be removed for development.

The wiring diagram of Fig. 3 shows the electrical circuits of the camera designed for operation on a 220-volt power circuit. When the drum is idling preparatory to exposure the contact C and the contacts controlled by both relays are closed. The two relay contacts are in series and when closed short-circuit the coils of the two electromagnets. When the contact of relay R_1 is opened by operating the armature manually or by means of the remote control circuit the contact of relay R_2 also opens and is held open until the contact C is opened. The relay R_2 is provided with a shunt to avoid having contact C interrupt the whole current in the 220-volt circuit for the purpose of terminating the action. The same consideration has led to the short-circuiting of the electro-

FIG. 5.



Film clamping device. Film clamped.

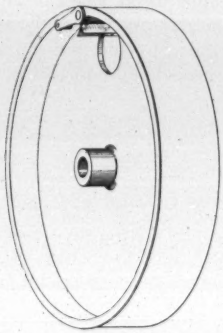
magnets in lieu of opening the power circuit as a means of de-energizing them. As soon as C opens, the contact of relay R_2 closes (the contact of R_1 already being closed), and the short-circuit across the electromagnets is restored.

The manner of clamping the film on the drum is of some importance, partly because at high speeds the centrifugal action presents a problem and partly because the desired record may come where the ends of the film are joined. Both difficulties are overcome in a fairly satisfactory manner by the following device: A hole h about three-eighths inch in diameter is drilled through the thick rim of the drum parallel to the shaft direction (see Figs. 4, 5 and 6),[1] and a saw-cut about one-thirty-second inch wide is made through the rim, the cut passing through the axis of the

[1] I am indebted to Major W. P. Wilson of the Coast Artillery Corps for the preparation of these figures.

hole. A split cylinder *C* terminating at one end in a small hand-lever fits the hole loosely. When a film is to be mounted, the slot in the cylinder is turned to coincide with that in the drum-rim and the end of the film is inserted into the channel formed by the lined-up slots. The drum is then rotated by hand, feeding the film into place. When the other end of the film is reached it is also inserted into the slot. The film is then adjusted to be reasonably taut by pulling with the hand the two film ends which

FIG. 6.



Relation of film clamping device to camera drum.

protrude from the lower end of the slot. Fig. 4 shows the situation at this point. A turn is then given the hand-lever which puts the film under tension on the drum and simultaneously locks it in place. Fig. 5 shows the film position after this operation is completed. The relation of the clamping system to the drum is illustrated by Fig. 6.

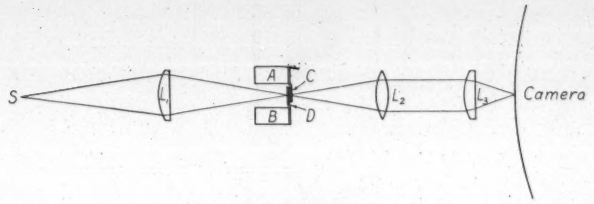
This method of clamping has been found quite adequate up to the highest film speeds which have been required, namely 100 feet per second. The ends of the film which serve for clamping are helpful in manipulating the film during development so that no portion of the film bearing the record needs to be handled. Finally, this method of clamping permits economy in the use of film. It serves equally well to clamp films of any width up to the full width of the drum. We have found a stock of film one inch, two inches, and four inches wide, convenient for general use in the laboratory. Frequently a one-inch film may be sufficiently wide

to obtain all the record that is wanted and in general will be sufficient for making adjustments. The economy which this possibility of using narrow films involves is obvious. If films specially cut for use in the camera are not available it has been found convenient to use standard moving picture film cut into suitable lengths.

SMALL-TIME SCALE APPARATUS.

The two prongs, *a* and *b* (Fig. 7), of a tuning fork have mounted upon them light metal vanes, *c* and *d*, which overlap and move freely past one another when the tuning fork vibrates. These vanes are perforated by slits parallel to the prong length. The slits are two or three-thousandths of an inch wide and are

FIG. 7.



Tuning-fork time scale system.

adjusted to line up when the fork is at rest. If then light from a source S is focussed on the slit by means of lens L_1 the slits transmit light when the fork is at rest and an image of the slit may be thrown upon the film by means of the lenses L_2 and L_3. If the fork is caused to vibrate light will be transmitted only while the fork prongs are passing through their equilibrium positions and no light will reach the film from the source during the other phases of the motion. As the film moves, therefore, images of the slit will be recorded at distance intervals which are determined by the frequency of the fork and the speed of the film. Two images are produced for each cycle of the fork. A 500-cycle fork will, therefore, give rise to 1000 time lines per second. The distance between two such lines is the distance the film advances during .001 second. A typical record of such a time scale is shown in Fig. 8.

In order that these time-scale lines shall be sharp it is neces-

sary that the duration of coincidence of the slits shall be short compared to the duration of non-coincidence. This condition is in some degree brought about naturally by the fact that the prongs have their maximum velocities in passing through the equilibrium positions. It is improved by vibrating the fork at large amplitudes.

It may be worth pointing out that if the point of exact registry of the slits is not in the equilibrium position the recorded time intervals for successive half-periods will not be the same. This

FIG. 8.

Typical time-scale record.

condition is remedied by adjusting the slits or sometimes more easily by using only the alternate timing lines on the film in making the measurements.

The advantages of a time scale of this character over a sinusoidal trace are rather obvious. To obtain any precision with the latter, it is necessary to draw chords parallel to the time axis and to bisect the chords in order to determine the exact position of the crests of the sinusoidal wave. The time lines may be looked upon as the equivalents of these bisectors experimentally obtained.

This method of obtaining a time scale did not originate in our laboratory. It was used by Prof. D. C. Miller,[2] in his phonodeik records and extensively by Doctors Curtis and Duncan[3] in connection with the G.E. oscillograph. Fig. 9 shows a 500-cycle

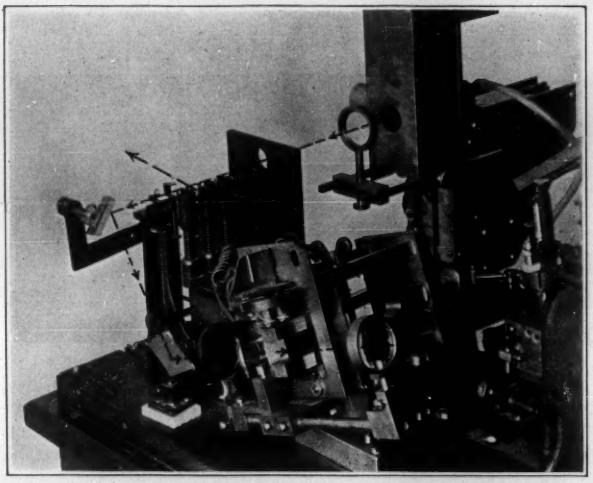
[2] D. C. MILLER, "The Science of Musical Sounds," Macmillan, 1916.

[3] H. L. CURTIS and R. C. DUNCAN, *Jour. Wash. Acad. of Sc.*, Vol. 9, p. 642, 1919; *Phys. Rev.*, 2nd Ser., Vol. 15, pp. 511, 512, 1920.

fork equipment mounted on the G.E. oscillograph of the Sound Laboratory. The optical arrangements can be easily followed by means of the light beam sketched into the figure. The electrical arrangements for driving the fork will be discussed later.

The incorporation of the timing system into the oscillograph as

FIG. 9.



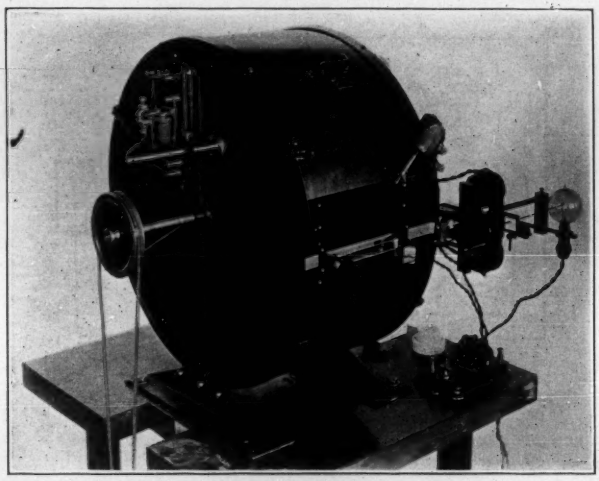
Tuning-fork equipment of G.E. oscillograph.

an integral part has the disadvantage of necessitating the equipment of each type of oscillograph. The difficulty is avoided by making the timing system a part of the camera. A unit of this kind is shown in Fig. 10. The upper plate of the part which functions both as lens housing and light shield has been removed and a light ray traced in to indicate the functioning of the optical system. For high film-speeds the concentrated-filament lamp shown in the figure must be replaced by an arc lamp.

Precise measurements require a close time scale, that is, many time index marks. In this way only can the errors due to unequal shrinkage of the film and non-uniform film speeds be reduced to

a minimum. In our work we have found one time line per centimetre adequate for most purposes. At a film speed of one metre per second a 50-cycle tuning fork will give this spacing. At a film speed of ten metres per second a 500-cycle fork will be required.

FIG. 10.



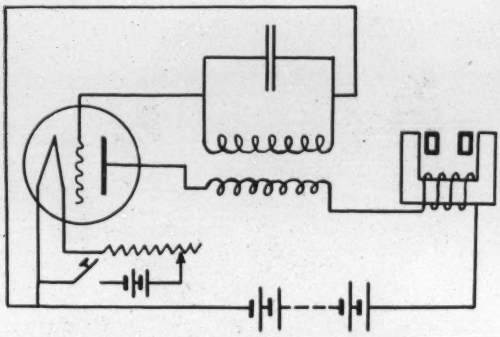
Camera with timing system incorporated.

It is well known that the difficulties of maintaining the vibrations of a tuning fork increase very rapidly with the frequency of the fork. Lord Rayleigh met the situation by driving a high-frequency fork by means of a low-frequency master fork. In this method the driving coils of the two forks are connected in series and the interruptions of the current are controlled by means of a contact on the master fork. The frequency ratio of the forks must be adjusted to be an integral number. Doctors Curtis and Duncan in this manner maintain the vibrations of a 500-cycle fork by means of a 100-cycle master fork.

The master-fork method of maintaining the vibrations of a

high-frequency fork has several practical disadvantages. The adjustment of the frequency ratio to an integral number is not permanent owing to a variety of causes, and the making of the adjustments is sometimes tedious, particularly when the frequency ratio is high. Furthermore the experimental difficulties increase very rapidly with the frequency for frequencies much above 500 cycles.

FIG. 11.



Idealized electron tube circuit for tuning-fork drive.

It occurred to us several years ago that the methods then available for obtaining sustained electrical oscillations by means of an electron tube might be available for maintaining the vibrations of a tuning fork. Our preliminary experiments had already been somewhat successful when we found that two British investigators, Eccles and Jordan,[4] had reached the objective and had published an account of their experiments. We have gradually developed this method of sustaining tuning-fork vibrations and are finding it remarkably reliable and convenient in connection with our time measurements.

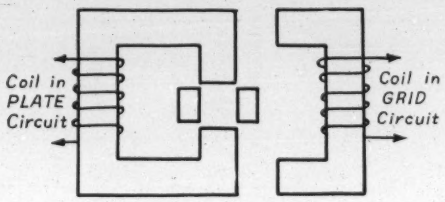
The idealized circuit arrangement for this type of tuning-fork drive is shown in Fig. 11 and the actual driving arrangement diagrammatically in Fig. 12. The d.c. component of the plate current magnetizes the laminated yoke with reference to which the fork prongs are so arranged that their motion will cause a

[4] W. H. ECCLES and F. W. JORDAN, *The Electrician*, Vol. 82, p. 704, 1919.

maximum change of the reluctance of the magnetic circuit. An adjustment is provided for varying the position, with respect to the yoke, of the laminated core which carries the grid coil. This control of the electromagnetic coupling between the grid and plate circuits constitutes an important practical advantage. The essentials of this type of tuning-fork drive have been described by Eckhardt, Karcher and Keiser.[5] A working unit is shown attached to the high-speed camera in Fig. 10.

With reasonably constant voltages the electron-tube drive is very satisfactory and the constancy of the frequency obtained has been checked in a large number of experiments.

FIG. 12.



Actual tuning-fork driving arrangement.

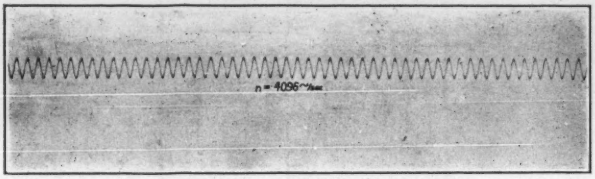
USES OF HIGH-SPEED OSCILLOGRAPH.

In Fig. 2 the camera is shown set up to obtain an oscillogram of the diaphragm motion of the loud-speaking telephone *Ph*. The linear motion of the centre of the diaphragm was converted into angular motion of a tiny mirror by the method used by Professor Webster in his phonometer. In this case the time-scale apparatus was not used, the wave form of the diaphragm motion being the point of interest. A record of the motion at a frequency of 4096 cycles is shown in Fig. 13. Records of the vibrations of a relatively massive system obtained in connection with a fatigue test of metals are shown in Fig. 14. In this case the system itself had sufficient angular motion to obtain the records shown. In Fig. 15 the camera is shown before the G.E. oscillograph of the Sound Laboratory and in Fig. 16 it is shown set up to coöperate with an Einthoven galvanometer. These figures indicate briefly the range of availability of the high-speed oscillograph camera.

[5] E. A. ECKHARDT, J. C. KARCHER and M. KEISER, *Phys. Rev.*, 2nd Ser., Vol 17, pp. 535, 536, 1921.

The precision of time measurement attainable is determined by the accuracy of the value used for the fork frequency and the character of the record obtained. The fork frequency is determined by recording the breaks of a break-seconds chronometer against the tuning-fork time scale. The frequency is then determined by counting the number of timing line intervals included between two chronometer breaks. When this is done the interesting fact comes to light that although the chronometer keeps excellent time on the average the individual seconds vary by several parts in a thousand. The same seconds interval, for example, that from the fifteenth to the sixteenth, as indicated by the

FIG. 13.



Oscillogram of diaphragm motion of loud-speaking telephone.

seconds hand, will repeat much more closely. To get an accurate value it is therefore necessary to measure every second in the minute and to repeat these measurements to check each second. In this manner the frequency of the fork may be obtained to one part in ten thousand.

The use of several different chronometers in such calibrations has indicated marked differences in the uniformity of the seconds intervals in different instruments and the method commends itself for the testing of the quality of break-circuit chronometer instruments.

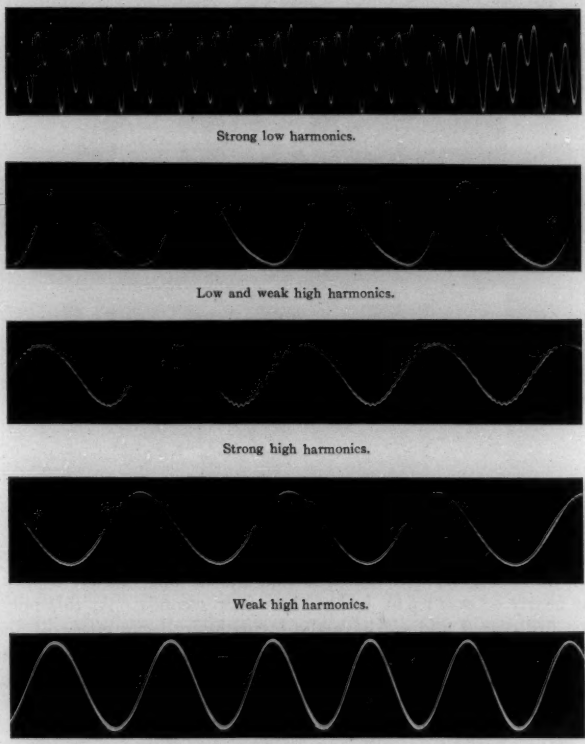
In closing, it may be of some interest to outline briefly one or two problems, the solution of which was facilitated by the use of the apparatus described.

COOLING TURBINE ON MACHINE GUN.

A proposal was made by someone that the air cooling of a machine gun could be improved by having a turbine propelled by the powder gases draw air past the barrel at an increased rate. The type of motive power was somewhat unusual and designers

wanted clues as to the efficient design of such a system. Several model turbines were built and tried and the question came up,

FIG. 14.



Strong low harmonics.

Low and weak high harmonics.

Strong high harmonics.

Weak high harmonics.

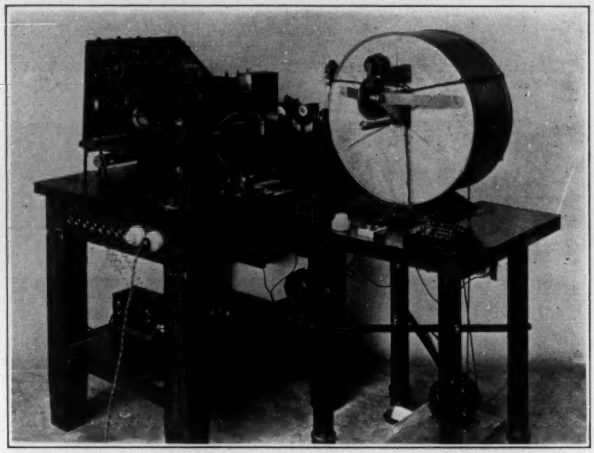
Satisfactory adjustment. Practically pure sine wave.

Oscillograms of flexural motion of massive mechanical vibrating system.

"What maximum speed do these turbines attain and in what time is it obtained?" After considering the problem we concluded that it would be feasible to have the turbine close a properly designed contact once every revolution and thus a record of the

duration of each revolution could be obtained. After some preliminary difficulties with the contact, satisfactory records were obtained from which the relation between the r.p.m. of the turbine

FIG. 15.



Camera with G.E. oscillograph.

and the time were deduced. The results of one such record are shown in Fig. 17. It indicates that the turbine reached a speed of nearly 24,000 r.p.m. in less than four seconds. At this point the fire ceased and we have the logarithmic decay curve of the rotating system coming to rest. Only a few of the many points obtainable from the records are indicated on the curve, these being sufficient to indicate the character of the acceleration.

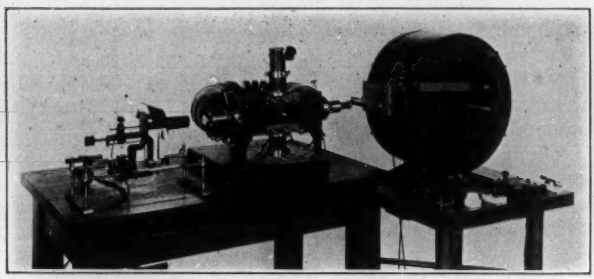
The rate of fire was slightly below ten shots per second, so that the curve relates to the firing of a burst of thirty-seven shots. The impulse due to each shot is readily discernible in the record by the markedly shorter time of the next succeeding revolution.

THE NAVAL OBSERVATORY—ANNAPOLIS TIME LAG.

As a matter of regular routine the Annapolis radio station sends out time signals twice daily, from 11 : 55 A.M. to noon, and

from 9:55 to 10:00 P.M. In the telephone of a radio receiving set one hears a sound of one frequency for approximately two-thirds of a second and another frequency for one-third of a second, alternating regularly very much like the "cuckoo" of a cuckoo clock. At the half minute one alternation is omitted and just before the minute five alternations. At the end of the five minutes ten alternations are omitted, that is, the pitch remains

FIG. 16.



Camera with Einthoven galvanometer.

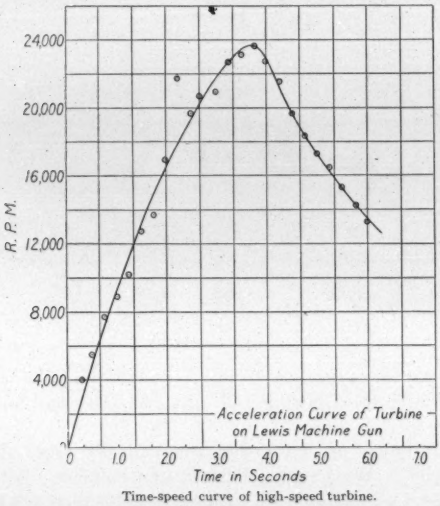
constant for ten seconds and then follows a long dash signal at the other pitch broadcasting 75th meridian noon and 10:00 P.M. at their respective times.

These signals are controlled automatically from the Naval Observatory at Washington, District of Columbia. Between the controlling clock and the radio transmitting set there are a number of relays which necessarily cause a lag of the radio signal behind the impulses of the controlling clock. In the affairs of everyday commerce a lag of a few hundredths of a second is of no importance, but there are cases in which such magnitudes need to be considered. One such case is the precise determination of longitude.

If the Annapolis noon signal is received at a place at precisely 1:00 P.M. local mean solar time we know that this place is 15° of longitude east of the 75th meridian. Two points, four geographical miles apart along the equator of the earth, have a difference in mean solar time of one second. An error of .01 second in time would make a change of something over 243 feet in the longitude

determination. In view of the development of automatic radio transmission and reception the times can be obtained so accurately that longitude determinations to within a few feet are being considered. There remains as a possible source of error the lag in transmission. This error can be largely eliminated if the lag is actually measured and the degree of its constancy established.

FIG. 17.



Time-speed curve of high-speed turbine.

In April, 1920, the U. S. Navy was coöperating with the British Admiralty in a longitude determination of this kind in Australia in which the 75th meridian and 75th meridian time were to serve as reference marks. Special time signals were sent out daily for a week from 2:00 to 2:15 P.M. The question of determining the lag was submitted to us and we made the attempt on less than a day's notice. The only oscillograph instrument available for the purpose was a string galvanometer which had been giving considerable trouble because of its inadequate damping, and this defect proved a considerable handicap since in the first records we found that the two phenomena, the interval between which we wished to establish, overlapped hopelessly on the record.

We overcame this difficulty by using an auxiliary clock during the transmission. The seconds beats of this clock were displaced with respect to those of the transmitting clock sufficiently to avoid this interference.

The following records were obtained:

1. Transmitting clock *vs.* auxiliary clock, five minutes prior to time signals.
2. Radio time signals *vs.* auxiliary clock.
3. Transmitting clock *vs.* auxiliary clock, five minutes after time signals.

To go into the results would exceed the limits of this paper. The values obtained, however, show that there are real variations in the lag which are of the order of .01 second, the lag itself being roughly .06 second. The observed variability indicates that in connection with precise longitude work the lags should be measured for each signal used in the determination.

Our work in this connection consisted simply in the experimental determination of the lag. We supplied the results to the U. S. Naval Observatory which was handling all other matters in connection with the longitude determinations.

In conclusion it is a pleasure to acknowledge the valuable contributions of my associates, Dr. J. C. Karcher and Mr. M. Keiser, who, no less than the writer, are responsible for the development of the apparatus and for its successful use in the solution of many interesting problems.

Eye Injuries in Industries.—The number of accidents resulting in the loss of one or both eyes by workers is very great, and strong efforts have been made to reduce them by the use of goggles. A good deal of experimenting has been done to secure satisfactory glass and some excellent forms have been produced. Workers are, however, not always favorable to their use, and run risks which often result in injury. In a recent bulletin of the National Committee for the Prevention of Blindness, issued from its office in the Russell Sage Foundation Building, it is stated that good work has been done in this line, and that the importance of the use of goggles has been impressed more widely upon workers. This is good news, for recent publications of the organizations interested in accident prevention have been to the effect that there has been a marked slackening of attention to the subject on the part of many industrial establishments. Safety provisions and insistance on the use of safety appliances have been discontinued in many places, and the working conditions allowed to

drift into the old careless methods of former years. This is to be regretted, but the cause is doubtless largely with the worker, who is very apt to become indifferent to the dangers of the occupation. "Familiarity breeds contempt" and also breeds indifference. It is stated in the bulletin above noted that in five years 3000 persons each lost an eye in the industries of Pennsylvania. The proper and persistent use of goggles would probably have diminished this figure very much. Full details concerning eye hazards in industries and the means of reducing or eliminating them will be presented in a revised edition of Bulletin 12, shortly to be issued by the National Committee. Several forms of posters, calling attention to dangers to the eyes and the methods of protection, have been distributed by the Committee.

H. L.

Egyptian Ink.—A. LUCAS (*Analyst*, 1922, xlvii, 9–15) has analyzed a sample of dried black ink which was contained in an inkstand of the time of Amenhotep III (sixteenth century, B.C.), and was approximately 3500 years old. The pigment in the ink was carbon; iron was absent. Carbon for ink has been made in Egypt by the destructive distillation of date stones, and by the incomplete combustion of incense. Inks, made from low-grade carbon and containing tar-like impurities, may yield a brown or partly brown color when used for writing. Iron inks apparently were first used during the seventh or eighth century, A.D. J. S. H.

Natural Sodium Compounds and Borates in 1921. (*Press Notice U. S. Geological Survey*, June, 1922.)—The production of natural sodium compounds in the United States in 1921 amounted to 25,000 short tons, valued at $894,000, according to reports of the producers to the United States Geological Survey. This was a decrease of about 41 per cent. in both quantity and value. The material marketed was sodium carbonate (soda ash) from Cartago and Keeler, Inyo County, California; sodium bicarbonate from Keeler, Inyo County, California; sodium sulphate (Glauber's salt) from Lake Point, Salt Lake County, Utah, and Casper, Natrona County, Wyoming; sodium borate (borax) from Trona, San Bernardino County, California; and trona (a double salt of sodium carbonate and sodium bicarbonate) from Trona, San Bernardino County, California.

The production of boron ores in 1921 was approximately 50,000 short tons, valued at $1,320,000. This represents a decrease of over 58 per cent. from the quantity shipped in 1920. The output was borax (sodium borate) from Trona, San Bernardino County, California, and colemanite (calcium borate) from Death Valley Junction, Inyo County, and Lang, Los Angeles County, California, and Dike, Clark County, Nevada. R.

ADDITIONAL NOTE ON SO-CALLED APLANATIC OPTICAL SURFACES AND LENSES.*

BY

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Professor of Physics, Columbia University, New York.
Member of the Institute.

SINCE the publication of my recent paper on "Aplanatic (or Cartesian) Optical Surfaces" [1] I have obtained, mainly from two sources, certain new information in regard to both the history of these surfaces and their modern applications, which would certainly have been included in the previous paper if I had been in possession of it at that time, and which seems to me to be of sufficient importance to warrant an additional note on the subject. The sources to which I allude are two well-known German works, one on the history of Optics published in 1838, and the other on modern optical instruments published nearly three-quarters of a century later in 1911; both of which I have often before had occasion to consult. Indeed, paradoxical as it seems, my very familiarity with each of these books is perhaps responsible for the fact that it had not occurred to me previously to suppose that either of them would throw any new light on the Cartesian surfaces and lenses.

The first work is Dr. Emil Wilde's "Geschichte der Optik" (Berlin, 1838) which contains a long chapter on Descartes, whose chief contributions to optical science are to be found in his famous treatise on "Dioptrique." [2] Now that the true law of refraction had been at last discovered, Descartes naturally regarded it as a matter of much importance to determine, theoretically at least, the most advantageous forms of the surfaces of optical glasses; and having proved that a cylindrical bundle of incident rays which were parallel to the axis could be converged accurately to a real focus either by a convex meniscus sphero-elliptic glass lens or by a planoconvex hyperbolic glass lens, he unhesitatingly recommended one of these forms as being decidedly superior to the

* Communicated by the Author.

[1] JOUR. FRANK. INST., 193 (1922), pp. 609-626.

[2] René Descartes: "Discours de la méthode pour bien conduire sa raison, et chercher la verité dans les sciences; plus La dioptrique, Les meteores et La géométrie," Leyde, 1637.

ordinary type of lens with both faces spherical, because under the same circumstances the ordinary type would necessarily have the fault of showing spherical aberration along the axis. In the same way also it was possible to design negative or divergent glasses which under the same conditions as before would likewise be free from spherical aberration, namely, a concave meniscus lens with an ellipsoidal surface concave towards the beam of parallel rays, the other surface being spherical, and a planoconcave hyperbolic lens placed so the parallel rays will fall perpendicularly on the plane face. Of the two types of lenses Descartes preferred the hyperbolic form as being both simpler and cheaper to manufacture. So confident was he of the enormous advantage to be gained by this method of construction that he believed it might even be possible to make a telescope which was so perfect optically that it would reveal the very details on the stars! Accordingly, he spent much mathematical ingenuity in trying to suggest mechanical contrivances for aiding opticians in grinding the requisite aspherical surfaces. When he was in Paris in 1628 he found there a man named Ferrier who actually succeeded in making for him a convex hyperboloidal glass surface; but as all his efforts to obtain a similar concave surface were in vain, Descartes was obliged to abandon the project of combining these lenses in a Dutch telescope (which is the only type of telescope which he discusses in the ninth chapter of the treatise above mentioned). Sir Constantijn Huygens, the father of Christiaan Huygens, was a friend of Descartes, and he endeavored to have these Cartesian lenses ground by some skilled Dutch opticians, equally without success. It is a little singular how much importance Descartes himself attached to this matter, especially as he knew that even if his hyperbolic lens were free from spherical aberration along the axis, it might not be as good as an ordinary lens for reproducing object-points which were a little off the axis. Moreover, the big difficulty in those early days when the telescope was still in its infancy was not so much the fault of spherical aberration as the far more serious matter of chromatic errors which not all the genius of Newton could overcome, so that he finally invented an entirely new kind of telescope to get around this fundamental trouble. The fact is that these Cartesian lenses may give exceedingly poor optical images even in monochromatic light. Nevertheless, by suitable combinations of a pair of them it is possible to re-unite at any prescribed point all the effective

rays belonging to a given point of an object, no matter whether the two points are real or virtual, one or both.

In my previous paper I remarked that Kepler, without knowing the true law of refraction, had somehow discovered the aplanatic property of an hyperbolic spheroidal refracting surface for rays proceeding in the denser medium parallel to the transverse axis of the hyperbola. In the same connection it deserves to be noted also that in proposition LX in his "Dioptrice" (Augsburg, 1611), Kepler explains with extraordinary perspicacity the mechanism of vision in the human eye and rightly conjectures that the image is focused on the sensitive surface of the retina, although J. B. Porta (1543–1615), who had compared the eye with a *camera obscura*, supposed that the image was formed in the crystalline lens itself. But Kepler even imagines that the crystalline humor is a convex lens with an hyperbolic posterior surface for the purpose of producing a more perfect convergence of the rays and consequently a sharper image on the retina.

The other book to which I alluded above is Dr. Alexander Gleichen's "Theorie der modernen optischen Instrumente" (Stuttgart, 1911) which has recently been translated in English.[3] The last chapter of this useful and original volume is on "Aplanatism," where, however, the author is careful to distinguish between a "Cartesian system" and an "aplanatic system" in the usual modern meaning of the latter term. Following Abbe, Gleichen used the word "aplanatic" to describe "a centered optical system which produces aplanatic imagery for all zones over a finite aperture," and which, therefore, besides being free from spherical aberration with respect to the axial point of the object, likewise satisfies Abbe's sine-condition. Gleichen refers to Descartes' "Dioptrique" and indicates how the equation of the Cartesian optical surface of the fourth degree in x and y is obtained; and likewise he calls attention to the fact that in certain special cases, particularly when one of the foci is infinitely far away, this equation reduces to one of the second degree and represents therefore a spheroid generated by the revolution of a conic section

[3] "The Theory of Modern Optical Instruments," by Dr. Alexander Gleichen, translated from the German by Messrs. Emsley and Swaine, and published for the Department of Scientific and Industrial Research by His Majesty's Stationery Office, London, 1918. (A new impression of this book has been issued perhaps within the past year.)

around the optical axis. "Beyond doubt," says Gleichen, speaking of these surfaces and other forms of aspherical optical surfaces, "aplanatic systems are destined to play an important part one day in technical optics as soon as methods have been devised for grinding the lenses with the same degree of accuracy with which spherical surfaces can be ground at present."

The aplanatic meniscus lenses with both faces spherical, which are described by Gleichen in detail, utilize the property of the well-known pair of aplanatic points of a spherical refracting surface. This remarkable pair of points was discovered first by Huygens and is mentioned by him in a letter to his former teacher Franc. van Schooten, in which he communicated the fact that under certain circumstances "one of the ovals which Descartes had conceived for re-uniting the rays reduces to the circumference of a circle."[4] Huygens himself has described fully the aplanatic meniscus lenses "of the first type," as Gleichen calls them.[5]

But by far the most interesting part of Gleichen's chapter on "Aplanatism" is the section entitled "Semi-aplanatic lenses made by Zeiss," in each of which one of the surfaces is plane or spherical while the other surface is aspherical. They are called "semi-aplanatic" because they are not completely aplanatic in the restricted meaning of the term; either the spherical aberration having been abolished for all zones and the sine-condition being satisfied for one zone, or *vice versa*. Gleichen gives a table with the numerical constants for twenty-four semi-aplanats of this kind, each of focal length $f = 100$, and also diagrams of six of them. A point to be noted in practically all these various types is the relatively small aperture and great thickness of the lens, which apparently limits its usefulness.

In conclusion Gleichen remarks again that "the employment of aplanatic, semi-aplanatic or Cartesian systems might be adopted more widely than heretofore with the development of the technique of glass working," and that it may be quite possible that "along these lines a revolution in technical optics lies before us." Several modern applications of so-called aplanatic optical combinations are

[4] "Œuvres complètes de Christiaan Huygens publiées par la Société Hollandaise des Sciences." Tome treizième, "Dioptrique" (La Haye, 1916), p. 48. See also Huygens's "Treatise on Light," translated by S. P. Thompson (London, 1912), p. 114.

[5] *Loc. cit.*, pp. 64–66.

instanced by Gleichen, namely, in "searchlight systems," "complex condensers for projection purposes," and "aplanatic field lenses;" not to mention the employment of "deformed" surfaces for special corrections, as, for example, in the so-called "Katral" spectacle lens and in the illumination system and receiving system of Gullstrand's ophthalmoscope.

DEPARTMENT OF PHYSICS,
COLUMBIA UNIVERSITY, NEW YORK,
May 8, 1922.

The Activation of Hydrogen.—Over a year ago Wendt and Landauer, of the University of Chicago, found that an unstable and active modification of hydrogen can be obtained by three methods: The action of alpha rays; alternating discharge at low pressures, and passage through the corona at ordinary pressure. Rays in the Schumann region produce no effect. The activity is not due to ions nor to atoms. A contraction in volume takes place which suggests an analogy to that which occurs in the activation of oxygen, and leads, therefore, to the view that the activated hydrogen is triatomic. The investigators have presented certain theories upon the subject. Independently of Wendt and Landauer a similar change in hydrogen was observed by Y. Venkataramaiah of the Indian Institute of Science at Bangalore. The experiments were made with detonating gas containing an excess of hydrogen. The mixture was submitted to the silent electrical discharge in an ozonizer and the mixture after leaving the ozonizer was passed through an alkaline solution of potassium permanganate. In the course of the experiment an electric spark accidentally occurred, which caused an explosion, destroying part of the apparatus, but the whole of the permanganate solution immediately turned green. It was at once suspected that this action might be due to a marked increase in the reducing power of the hydrogen, inasmuch as ordinary hydrogen brings about such a change very slowly. A Hofmann eudiometer was filled with an alkaline solution of the permanganate and a few cubic centimetres of the detonating gas with excess of hydrogen were introduced. Electric sparks were produced in the mixture and the solution turned green. Further studies showed that an alkaline solution of indigo is bleached, ferric chloride is turned into ferrous, potassium nitrate into nitrite, arsenous acid into hydrogen arsenide, potassium perchlorate into potassium chloride. Other similar reactions were observed.

References to the literature show that in 1913 Sir J. J. Thomson made observations indicating the production of particles having an atomic weight of three, presumably hydrogen. Duane and Wendt found in 1917 that the influence of alpha particles from radium ema-

nation produces a contraction of volume in hydrogen. In 1912, Langmuir produced an active modification of hydrogen by heating a filament in the gas at low pressure. Further observations on this modification have been presented by the Indian investigators, and the American observers are also working along this line. The results of the investigation in India are published in the bulletin of the Science Association of the Maharajah's College, Vizianagram.

H. L.

Standard Colors for Traffic Signals.—A conference on the standardization of colors for traffic signals was recently held in New York under the auspices of the American Engineering Standards Committee. Representatives were present from practically all of the national engineering societies, safety associations, electric and steam railway interests, automobile dealers, manufacturers and users associations, police and traffic departments, insurance companies, and several departments of the federal government.

It was agreed unanimously "that there should be national uniformity in the use of colors for signals," and that the detailed technical work involved in bringing this about should be by a sectional committee under the auspices of the American Engineering Standards Committee. Included in the scope of the work were the following:

The use of colored lights on all highway vehicles.

Their use on all signals along highways and at curbs, both permanent and temporary.

Their use for highway crossing signals for steam and electric railways.

A coördinated relation of color, form, position and number of signals.

A coördinated relation to system of flashing, moving or other similar lights.

Colors for non-luminous as distinguished from luminous signals.

Recommendations on the use of colors for emergency exit signals.

Methods of specifying or defining colors for signal purposes.

Any other closely related matters which, in the opinion of the sectional committee, form a part of the subject to be considered.

A suggestion that yellow light be used in place of red for the tail light of automobiles brought forth a spirited discussion.

The conference did not advocate the substitution of green for red as a danger signal, as was erroneously reported in some daily papers due to misinterpretation of discussions. On the contrary, the ideas expressed at the conference were emphatic that red should be used to indicate danger and for no other purpose. In conformity therewith, it was suggested that green be substituted for red as the color for lights for emergency exits of public buildings as indicating paths that lead to safety.

H. L.

CONTRIBUTIONS TO THE CHEMISTRY AND TECHNOLOGY OF GELATIN AND GLUE.*†

BY

ROBERT HERMAN BOGUE, Ph.D.

Industrial Fellow of the Mellon Institute of Industrial Research of the University of Pittsburgh, and Research Chemist for Armour and Company of Chicago.

In the first of these, the gelatin solutions were subjected to viscosity measurements at varying temperatures and under varying speeds of rotation (using the MacMichael viscosimeter) to determine if evidence of plastic flow could be observed. It was found that in a 25 per cent. solution, plastic flow first became manifest at about 34° C. This was indicated by the fact that an extrapolation of the viscosity-r.p.m. curves met the axes at the origin at temperatures above 34°, but below this temperature the intercept occurred at increasing distances from the origin on the viscosity axis. This is illustrated in Fig. 13. At lower concentrations the transitional temperature appears also to be lower.

The other series of experiments consisted of a measurement of the change in viscosity with time of gelatin solutions at varying H-ion concentrations and under different degrees of purity. The data, illustrated in Fig. 14, show that at 35° C. the viscosity of a normal gelatin decreases with time except at *pH* 4.7. The viscosity of the ash-free sample increased slightly with time at 35°, but was constant at 37°.

The first of these experiments indicates that the transition from the sol to the gel condition is a gradual and not a sudden change, such as occurs for example when a crystal of benzol changes to the liquid phase, and that the measurability of the change is a concentration variable. The second experiment indicates that there are several factors influencing the effective volume of the gelatin in the solution. These include the H-ion concentration, the amount and nature of the inorganic ions present, and the products of gelatin hydrolysis.

In 1920, the writer [63] outlined his views upon the structure

* Communicated by Dr. E. R. Weidlein, Director, Mellon Institute of Industrial Research of the University of Pittsburgh.

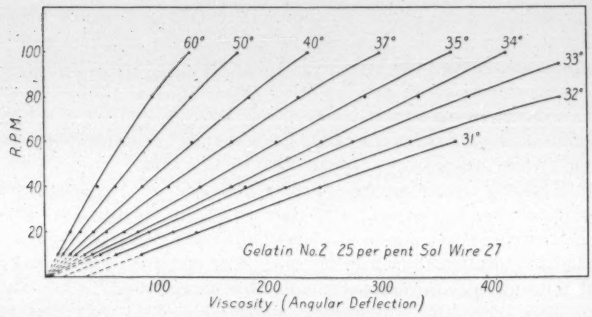
† Concluded from JOUR. FRANKLIN INST., June, 1922, p. 825.

[63] R. H. Bogue: *Chem. Met. Eng.*, 23 (1920), 61.

of gelatin-water systems. There has since that time been so much work of a more or less confirming character that it seemed desirable to restate the theory, and to add thereto further postulations based upon recent work.[64]

Gelatin sols appear to consist of slightly hydrated molecules united together into short threads[65] resembling streptococci. These threads are probably very short, but should be capable of exhibiting mechanical elasticity roughly proportional to their length. Procter[66] thinks that at 70° C. the solution becomes probably nearly molecular.

FIG. 13.



Viscosity-plasticity curves.

A lengthening of these threads seems to take place as the temperature falls, and at the same time the water-absorbing power of the gelatin increase.[67] This accounts for the rapid increase in the viscosity with drop in temperature. At temperatures above 40° C. the change in length of thread or water absorption, per unit change in temperature, is small, but at 30°–20° the change

[64] R. H. Bogue: *Loc. cit.*

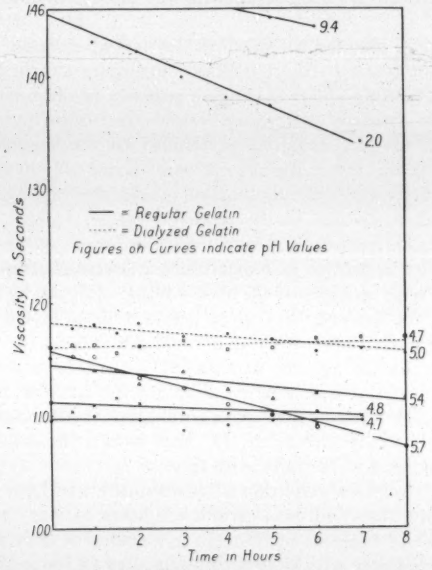
[65] J. Loeb has found the assumption of a few united molecules to account for the differences in the osmotic pressures of calcium and sodium gelatinates. (*J. Gen. Physiol.*, 1 (1919), 496.)

[66] H. R. Procter: *Cf.* Ref. 40, p. 41.

[67] Whether or not this is real hydration is undetermined. McBain and Salmon (*J. Chem. Soc.*, 119 (1921), 1374) have reported an increase in hydration of soap upon a lowering of the temperature. H. C. Jones (*Z. physik. Chem.*, 74 (1910), 325) has shown that the hydration of molecules and ions increases with a fall in temperature.

is very great. A solid jelly will result only when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity seems to depend on the relative amount of free solvent in the interstices of these aggre-

FIG. 14.



Change in viscosity with time at varying *pH* 2 per cent. solution, 35°C.

gates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is probably dependent upon the length and number of the catenary threads. A solution, or change from the gel to the sol form, may result only through the reversal of these processes. That is, a release of a part of the water retained by the heavily swollen molecules, and a partial disintegration of the long enmeshed fibrils of the gel. Any tendency on the part of the fibrils towards an orientation would imply an attractive force between

them which would result in a shrinkage. This becomes manifest in syneresis. That some such orienting force does exist is indicated by the lenticular form of bubbles that are generated within gels. The degree of swelling that may be produced in cold water or electrolyte solutions is determined by osmotic forces, as described by Procter, and may be controlled by observing the principle of the Donnan Equilibrium as shown by Procter and by Loeb.

It appears that the colloid fibril consists at elevated temperatures of but a few partially hydrated molecules attached to each other, and floating about as discrete particles in the solvent. An increase in viscosity with time would then signify either an increase in the size (length) or number of the threads, or an increased volume due to the absorption of water or hydration. At elevated temperatures, the equilibrium is evidently rapidly attained. This seems to be due to the relatively small changes that are induced in the particle size and degree of water absorption or hydration by variations in temperature at *elevated temperatures*, and to the high mobility of the free solvent. But as the temperature falls, the amount of change per unit drop in temperature increases rapidly, and with this a rapid decrease in the mobility of the solution through the withdrawal of the solvent by absorption or hydration. The time required for the colloidal molecule-fibrils to reach a state of complete equilibrium with the solvent is consequently vastly increased. In other words, the solution will show an increase in viscosity with time.

Under any given condition of temperature and hydrogen ion concentration there will be a certain condition of viscosity which the system will attain at equilibrium. A temperature at which no change in viscosity with time occurs indicates an immediate equilibrium condition, but this temperature will vary with different hydrogen ion concentrations and with different degrees of purity of the sample. It is in no way indicative of a critical equilibrium temperature between the sol and gel forms, but is rather only a point on a continuous curve. This may be expressed by the equation:

$$\eta_{pH} = K / f(T),$$

where η_{pH} is the viscosity at equilibrium at any given pH, $f\ (T)$ is some function of the temperature, and K is a constant. On

account of the length of time required to attain equilibrium, and the difficulty of eliminating completely all other influences as hydrolysis due to the prolonged action of water, electrolytes, or bacteria, the exact measurement of η_{pH} is uncertain, except where the conditions have been met for existence of an equilibrium *immediately*. This is the condition encountered where that temperature is obtained at which no change in viscosity with time is observed.

The idea of a gradual rather than an abrupt change on passing from the sol to the gel form is further indicated by the finding of Walpole [68] that the refractive index of a gelatin-water system is a linear function of the concentration, and if plotted against the temperature shows no discontinuity at any point between the liquid sol and the rigid gel. And McBain [69] has reported that the sol and gel of soaps differ only through the mechanical rigidity and elasticity of the gel form.

The writer [70] has shown that the gel consistency is proportional to the undegraded protein present in a gelatin or glue. It follows, therefore, that the unhydrolyzed gelatin possesses a much larger water-absorbing capacity than the proteoses or peptones. It was also pointed out that the viscosity varied apparently with the size of the colloid aggregate in the solution. The present theory demands that viscosity vary with the degree of water absorption (measured by the rigidity of the gel) and with the size (length) and number of the colloid fibrils (measured by the elasticity of the gel),[71] and also, of course, with the concentration of the solution. The "melting point" was shown [72] to be determined by the protein content and was found to give a "grading" lying between that resulting from measurements of gel strength and of viscosity at high temperature (60° C.). Since it has been indicated [73] that "melting point" is in reality only a transitional period between the sol and gel forms, and that the transition involves only a change in the water-absorbing capacity and the length and number of the colloid molecule-threads, it follows if the above is true that any measure of "melting point" will indi-

[68] G. S. Walpole: *Kolloid-Z.*, **13** (1913), 241.
[69] M. E. Laing and J. W. McBain: *J. Chem. Soc.*, **117** (1920), 1506.
[70] R. H. Bogue: *Chem. Met. Eng.*, **23** (1920), 105.
[71] See Apparatus of S. E. Sheppard: *J. Ind. Eng. Chem.*, **12** (1920), 1007.
[72] R. H. Bogue: *J. Ind. Eng. Chem.*, **14** (1922), 435.
[73] R. H. Bogue: *J. Am. Chem. Soc.*, on press.

cate a resultant between the effects of hydration or water absorption and of length or number of threads, or, differently expressed, a resultant between gel strength and viscosity at high temperature, which is exactly in conformance with the data reported in an early paper.

Fischer [74] is of the opinion that "the phenomena of hydration (swelling) and of 'solution' while frequently associated are essentially different. Hydration is to be regarded as a chance through which the protein enters into physico-chemical combination with the solvent (water); 'solution,' as an increase in the degree of dispersion of the colloid." This is in satisfactory agreement with the ideas expressed above, for although we do not consider that a true solution may exist at low temperatures on account of the heavy hydration or water absorption, yet the change in a jelly upon conversion to a liquid seems to involve a disintegration of the colloid aggregates (increase in degree of dispersion) as well as lessening in the degree of hydration or water absorption.

The recent work of McBain and his collaborators [75] on the structure of the sol, gel, and curd of soaps is of especial interest and is in agreement with the theory outlined. They report that in soaps "the colloidal particles in the sol and gel are the same, but whereas in the former they are independent, in a fully formed gel they stick together, probably to form a filamentous structure." They add further that "the sol and gel differ only through the mechanical rigidity and elasticity of the gel form." That is precisely what would follow in gelatin sol and gel from the postulations made above, and is further indication of the gradual nature of the changes which obtain in the sol-gel equilibrium. They state as their belief that a filamentous structure is the general characteristic of soap gels as distinguished from sols. They regard these filaments, however, as normally amicroscopic in size, while in the curds a probably crystalline formation is produced. In gelatin systems the curd or crystalline condition is not known. Harrison,[76] however, reports that he has obtained ultra-

[74] Martin Fischer and W. D. Coffman: *J. Am. Chem. Soc.*, 40 (1918), 304; Martin Fischer: "Soaps and Proteins," New York (1921), 219.

[75] Mary E. Laing and J. W. McBain: *J. Chem. Soc.*, 117 (1920), 1506; W. F. Drake, J. W. McBain, and C. S. Salmon: *Proc. Roy. Soc.* London, A 98 (1921), 395.

[76] W. Harrison: *Cf.* Ref. 40, p. 57.

microscopic photographs of gelatin and cellulose gels which showed them to consist apparently of "minute portions joined together in a somewhat irregular manner."

Barratt[77] has accepted the fibrillar structure theory as representing most adequately the properties of elastic gels, and reports that ultramicroscopic examination, when it reveals any structure at all, shows the gel to consist "not of liquid droplets enclosed by (solid) septa, as the honeycomb theory requires, but of a mass of intersecting fibrils, which run perfectly straight, and are united at their points of intersection." He concludes that "the real structure of these gels is a fibrillary network, at first amicroscopic and later becoming ultramicroscopic."

A gradual and regular change in properties accompanying the transformation of the sol to the gel or the gel to the sol also supports the theory of structure that has been set forth. This gradual and regular change is indicated by the viscosity-plasticity studies described; by the finding of Walpole[78] that the refractive index of a gelatin-water system is a linear function of the concentration, and when plotted against the temperature no break occurs in the region of gelation; by the conclusion of McBain[79] that the sol and gel forms of soap differ only in the formation of a filamentous structure which accounts for the different properties of the latter; by the reports of C. R. Smith[80] that mutarotation exists between the temperature 15° and 30° C.; by the demonstration of Arrhenius[81] that the conductivity of salt-gelatin-water systems was the same in the sol and the gel conditions; and by the findings of Thomas Graham[82] that the rate of diffusion in dilute gels was approximately the same as in pure aqueous solutions.

It is also of interest to note that dibenzoyl-*l*-cystine which has recently been described by Gortner,[83] and which is capable of forming an elastic gel at concentrations as low as 0.2 per cent.,

[77] J. O. W. Barratt: *Biochem. J.*, 14 (1920), 189. *Cf.* Ref. 40, p. 49.

[78] G. S. Walpole: *Kolloid-Z.*, 13 (1913), 241.

[79] M. E. Laing and G. W. McBain: *Loc. cit.*

[80] C. R. Smith: *J. Am. Chem. Soc.*, 41 (1919), 146; *J. Ind. Eng. Chem.*, 12 (1920), 878.

[81] S. Arrhenius: *Ofvers. Stockh. Akad.* (1885), No. 6, 121.

[82] Thomas Graham: *Phil. Trans. Roy. Soc.*, 1864.

[83] R. A. Gortner: *J. Am. Chem. Soc.*, 43 (191), 2199.

was also shown by an ultramicroscopic examination to consist, in the gel condition, of a fibrillar structure.

Experiments upon the influence of H-ion concentration and of inorganic ions on the swelling, viscosity, jelly consistency, foam, turbidity, and alcohol number were shown to give data which supports the theory presented. The occlusion theory of Loeb, [84] which has already been described, is also found to be in harmony with the views presented.

Notwithstanding the very considerable progress that has been made in the last ten years in the fields of the chemistry and technology of gelatin and glue, there remains much for the immediate future to accomplish. A beginning has been made which will insure a momentum to this branch of chemistry for a long period to come, but problems of importance await solution at every turn, and if there be competent chemists who are searching for interesting research, we invite them to a consideration of gelatin and glue.

The Disappearance of Gas in the Electric Discharge. Research Staff of the General Electric Company, Ltd., London. (*Phil. Mag.*, May, 1922.)—Hydrogen and nitrogen behave in very nearly the same way in respect to disappearance in the electric discharge. In the case of these two gases when phosphorus is present the following conclusions are reached:

1. "The nature of the discharge has little direct effect upon the amount of gas absorbed."

2. "The form of vessel is important only in so far as it affects the area of the wall exposed to the discharge."

3. "The pressure of the gas during absorption has no affect within wide limits on the amount absorbed."

4. There is a very irregular connection between the amount of phosphorus present and the amount of gas absorbed. In general the two increase together, but not always.

5. The condition of the glass walls of the vessel makes no difference, but the deposit of certain salts or of tungsten on the walls greatly increases the absorption.

A suggested explanation ascribes the absorption to an electrically polarized solid layer on the surface, in one case of phosphorus, in another of the salts. When negatively charged ions approach the surface they are attracted and held fast. In the case of absorption by glass alone it may be that its surface layer is polarized by the discharge. It will be noted that much more is known about the phenomenon than about its causes. G. F. S.

[84] Jacques Loeb: *J. Gen. Physiol.*, **3** (1921), 827; **4** (1921), 73, 97.

A SOURCE OF LIGHT GIVING A CONTINUOUS SPECTRUM IN THE ULTRA-VIOLET.*

BY

W. H. FULWEILER AND JAMES BARNES.

Members of the Institute.

In our observations on the ultra-violet absorption spectra of some hydrocarbons and petroleum oils, we have used a source of light which has given such satisfactory results that a brief description of it may interest others who are working in this field of spectroscopy.

The source of light which has been used very extensively by investigators is the condensed spark between electrodes of various metals and their mixtures. While the manipulation of this source is very simple, it has the great disadvantage that its spectra consists of many bright lines superimposed on a more or less continuous background.

When using this source of illumination it is difficult to determine the edges of absorption bands when they are close to or coincident with a bright line so that it is frequently necessary to use more than one metal in order to eliminate this difficulty.

It is obvious that a source of illumination that would give a continuous spectrum in the ultra-violet would not only be very much more convenient but should enable the absorption bands to be more accurately located.

Grebe [1] seems to have been one of the first to use a continuous source of illumination in the ultra-violet for spectroscopic work. In his apparatus, the spark was passed between aluminum electrodes under flowing water. The aluminum electrodes give off a considerable amount of oxide and wear away quite rapidly so that they must be continually adjusted.

Howe [2] employed the high-frequency oscillations set up by means of a Tesla coil to produce a spark between aluminum electrodes placed under distilled water, and he states that this source

* Communicated by the Authors.

[1] *Zeitschr. f. wiss. Photo.*, 3, 376, 1905.

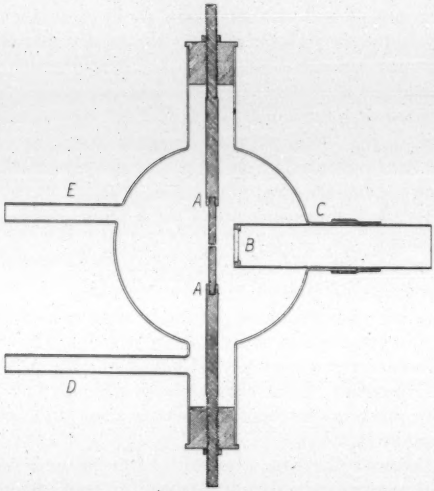
[2] *Phys. Rev.*, **8**, 674, 1916.

gives a continuous spectrum that extends with long exposures to 2100 A. U.

Strachan [3] has used high-frequency oscillations with a Tesla coil and brass electrodes under water. Using from 4 to 6 kilowatts in the primary of the transformer, he secured a very satisfactory continuous spectrum extending to 2200 A. U.

After trying the spark with a number of alloys we set up

FIG. 1.



apparatus similar to that used by Howe, but did not secure results desired. After making a number of modifications, the principal one being the omission of the Tesla coil, we finally secured a set-up which gave very satisfactory results.

Method.—The final modification of the apparatus is shown in Fig. 1.

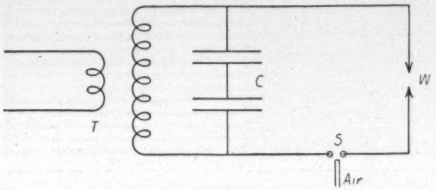
The electrodes A consisted of tungsten rods 3.5 mm. in diameter. These are mounted in brass rods which screwed into solid rubber stoppers. The stoppers were sealed with hard wax on the

[3] E. K. Strachan, private communication.

side tubes of a pyrex glass bulb of about 500 c.c. capacity. By means of the threads on the brass rods the position of the spark gap relative to the quartz window B, and also the length of the gap could be easily adjusted. We found under the electrical conditions used that a spark length of about ½ mm. was the most satisfactory. The quartz plate B, 16.5 mm. diameter, was fixed by washers and screw cap to the end of a brass tube which slipped through the side tube C of the vessel and was held in position by a rubber tube. The spark gap was about 1 cm. from the window and about 2 cm. below the surface of the water which flowed in through the tube D and out at E.

For the production of the spark we employed a G. E. X-ray transformer, type K, using 15 amperes from the 110 volt A. C.

FIG. 2.



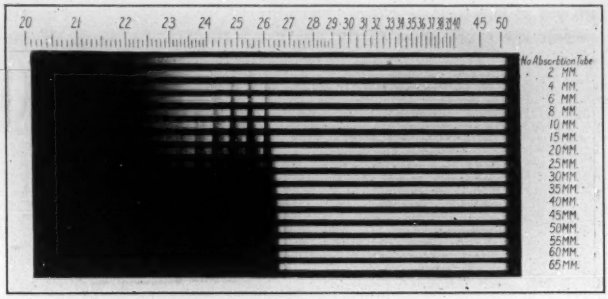
mains on the primary coil. A mercury interrupter which made and broke a D. C. current about 120 times a second was also employed. For capacity, two Leyden jars of about .001 m.f.d. each were used. A zinc spark gap upon which a blast of air was directed was placed in series with the tungsten spark. Fig. 2 shows this electrical circuit where T is the transformer; C, the capacity; S, the external spark gap and W, the tungsten spark.

The choice of tungsten for the electrodes was made after a careful trial of aluminum, brass, iron, nickel, carbon and molybdenum. The tungsten gave more light in the shorter wavelengths and required very much less adjustment.

Using 1.6 k.w. in the primary of the transformer, the tungsten electrodes disintegrated very slowly compared with aluminum poles used under exactly the same conditions. The spark length had rarely to be adjusted during a complete set of observations as for example the set shown on Fig. 3.

Results.—As illustrating the results obtained with this source of illumination, we have reproduced on Fig. 3, a positive from one of our negatives showing the absorption bands of 0.1 per cent. solution of benzene in ethyl alcohol. The lengths of solution used are indicated on the side of the plate. It is unfortunate that reproduction does not do justice to the very fine detail that is present in the original plate. This photograph is taken with a Hilger quartz spectrograph, type E-2, using a slit of 0.05 millimetres with

FIG. 3.



two minute exposure on a Seeds 23 plate. One and six-tenths k.w. were used in the primary of the transformer.

The top exposure in Fig. 3 with no absorption tube indicates the uniformity of the illumination. In the original negative the spectrum extends to 2050 A. U. In connection with the absorption bands of benzene, the original negative shows eleven bands, some of these are lost, however, in the reproduction.

CHEMICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, May 3, 1922.

Soy Bean Oil.—W. B. SMITH (*Jour. Ind. Eng. Chem.*, 1922, xiv, 530–531) has analyzed several samples of soy bean oil. He finds that an oil with an iodine number of 134 has approximately the following composition: Linolenic acid, 2 to 3 per cent.; linolic acid, 55 to 57 per cent.; oleic acid, 26 to 27 per cent.; saturated acids, 9 to 10 per cent. J. S. H.

THE RESOLUTION OF THE Kα DOUBLET IN THE POWDER METHOD OF X-RAY CRYSTAL ANALYSIS.*

BY

L. W. McKEEHAN, PH.D.

Research Physicist, Engineering Department, Western Electric Company.

In the powder method of X-ray crystal analysis, suitably oriented crystals large enough to give separately distinguishable spots on the photographic film reflect the two wave-lengths of the Kα doublet—$K\alpha_1$ and $K\alpha_2$—at slightly different angles, so that these spots are also doublets.

Using a copper anti-cathode, W. Gerlach [1] reported that the separation of such doublets was only about half of the value which he expected from the known values of the wave-lengths. As I mentioned in a recent paper,[2] the positions of double spots in my photographs taken with a molybdenum anti-cathode were in rough agreement with the equations

$$\lambda_1 = 2d \sin \theta_1 \qquad (1)$$

$$\lambda_2 = 2d \sin \theta_2 \qquad (2)$$

wherein $2\theta_1$ and $2\theta_2$ are the angles which lines joining the centre of the sample to the centres of the spots make with a line joining the centre of the source with the centre of the sample.

In a recent note, F. Kirchner [3] has explained the small values for spot separations obtained by Gerlach as theoretically justified, and Gerlach [4] has recalculated the values of wave-length difference, $K\alpha_2 - K\alpha_1$, from his measured separations, getting very good agreement with experimental and theoretical results for copper and nickel radiators.

This leaves my results apparently out of line with both theory and experiment, but it is quite easy to show that there is no real contradiction, both results agreeing with a complete theory of the phenomenon.

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* Communicated by Brigadier General John J. Carty, D. Eng., Associate Editor.

[1] W. Gerlach, *Phys. ZS.*, **22**, 557–559 (1921).

[2] L. W. McKeehan, FRANK. INST. JOURN., **193**, 231–242 (1922).

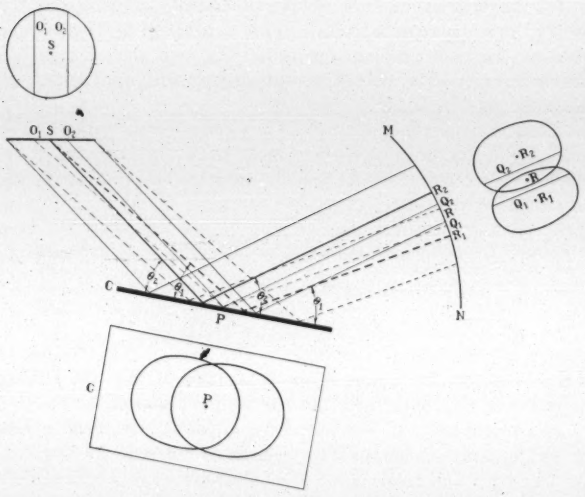
[3] F. Kirchner, *Phys. ZS.*, **23**, 114 (1922).

[4] W. Gerlach, *Phys. ZS.*, **23**, 114-120 (1922).

In Fig. 1 let S be a plane source of any finite extent giving X-rays of two wave-lengths, λ_1 and λ_2 ($\lambda_2 > \lambda_1$). Let C be a group of crystal lattice-planes with primitive interval d. There will be two reflected beams, as shown, where equations (1) and (2) determine the values of θ_1 and θ_2.

If the crystal is of unlimited area each point of the source will

FIG. 1.



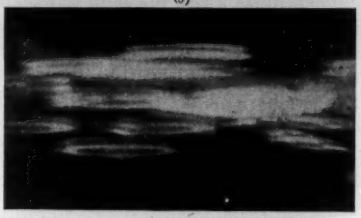
give a complete circular cone of reflected rays with its apex at the ordinary mirror image of the chosen point in the plane C, and cutting the film MN in a curved line. With long crystals of tungsten, such traces have been obtained about 2 cm. long and showing a slight convexity on the less deflected side, as they should, considering the actual shape of MN, which was a circular cylinder centered at P. An enlarged reproduction of such traces is given in Fig. 2 (a). The double character of these long traces is evident, but they are not well enough defined for accurate measurement of the separation.

Smaller crystals give patterns on the film which show clearly the distribution of intensity among the points of the source which,

FIG. 2.

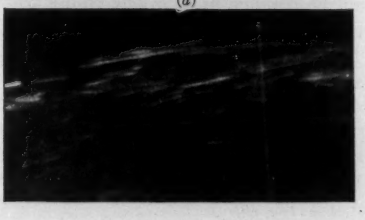
(a)

(b)



(c)

(d)



Actual width of fields is 2.0 cm.

by pin-hole photographs was found to be a brilliant annulus with a relatively non-emitting centre. The two pairs of parallel projections indicated in Fig. 1 give rise in the film to two very nearly similar elliptic bands, the ratio of the major to the minor diameter of each ellipse being about 8 and the major diameter being about 0.6 cm., the same as the diameter of the circular source. A pair of such ellipses is shown in Fig. 2 (*b*).

These ellipses are not sharply defined except near the ends of their minor axes, because of the width of the crystal. The wider the crystal the longer is the trace of the cone of reflected rays which were emitted at a point on the source, and the "image" of the source is built up by the superposition of these parallel lines of limited length exactly as a real image in any optical system is built up by the superposition of the diffraction patterns due to the points of the source. An additional cause of blurring is the thickness of the crystal perpendicular to the reflecting planes, but this was not serious with the thin sheets of metal which I found most convenient for other reasons.[5]

Inspection of Fig. 1 shows that the arc length R_1R_2 between the centres of the two elliptical spots is given by

$$R_1R_2 = (SP + PR)(\theta_2 - \theta_1) .$$

In the actual apparatus SP and PR were nearly equal, so that to a first approximation

$$R_1R_2 = 2PR(\theta_2 - \theta_1) .$$

Crystals too small to intercept both of the reflectable beams in their entirety will give rise to defective ellipses, one or both being cut off by lines due to the boundaries of the crystal, so that the ellipses may be cut off by lines in any position with respect to the axes of the ellipse. An example of such defective ellipses is given in Fig. 2 (*c*). It is clear that with the disposition shown in Fig. 1 it would be possible to have one ellipse complete and the other reduced to a narrow arc on the side nearest to the unaffected spot. If the beams do not overlap on C one spot of the pair may be wholly absent.

Carrying the reduction in size of the reflecting surface still farther, a very small area at P, in the region common to the two beams, will reflect only rays from O_1 and O_2, to Q_1 and Q_2, respectively, so that the two ellipses are now represented simply

[5] L. W. McKeehan, *Loc. cit.*

by two chords, that is, by two very narrow parallel lines on the film. This is the case obtained by Gerlach, and occurs in my experiments with metals where special heat treatment has permitted the formation of very small crystals free from strain. A region showing several such pairs of lines is shown in Fig. 2 (*d*). An area outside the region common to the two beams cannot give rise to two lines of this sort, so that single lines are also of frequent occurrence.

The arc length Q_1Q_2 between the lines due to reflection from the same tiny crystal is given by

$$Q_1Q_2 = PR\,(\theta_2 - \theta_1)\,,$$

half the approximate value found above for R_1R_2. If differences in wave-length are to be determined this may be put in the rigorous form

$$\lambda_2 - \lambda_1 = \frac{\lambda_2 + \lambda_1}{2} \cot \frac{\theta_2 + \theta_1}{2} \tan \frac{\theta_2 - \theta_1}{2}$$

or for small values of $(\theta_2 - \theta_1)$

$$\lambda_2 - \lambda_1 = \frac{\lambda_2 + \lambda_1}{2} \cdot \frac{Q_1Q_2}{PR} \cot \frac{\theta_2 + \theta_1}{2}\,.$$

In the case of molybdenum, Duane [6] gives

$$\lambda_2 = K\alpha_2 = (0.71212 \pm 8) \times 10^{-8} \text{ cm.}$$

$$\lambda_1 = K\alpha_1 = (0.70783 \pm 7) \times 10^{-8} \text{ cm.}$$

so that $$\lambda_2 - \lambda_1 = (4.29 \pm 11) \times 10^{-11} \text{ cm.}$$

My measurements upon a single photograph where many sharply defined pairs of lines occurred gave

$$\lambda_2 - \lambda_1 = (4.36 \pm 5) \times 10^{-11} \text{ cm.}$$

in satisfactory agreement with Duane's value. Gerlach's values computed in this way agree equally well with previously published values of comparable accuracy for copper and nickel.

SUMMARY.

Double spots due to reflection of two nearly equal wave-lengths by the same crystal may be of two kinds.

(1) Fine parallel lines are due to reflection of rays from different parts of the source by a very small crystal. The separa-

[6] W. Duane, *Nat. Res. Counc. Bull.*, 1, 383–408 (1920).

tion of such lines depends only upon the difference in wave-length, the mean wave-length, and the mean of the observed angles of reflection. They are excellent objects under the microscope and give an accurate method for determining small differences in wave-length.

(2) Projected images of the whole source are due to reflection of rays from each point of the source at different points in the crystal. The separation of such images depends upon the difference in wave-length, the mean wave-length, the mean of the observed angles of reflection and upon the ratio of the whole path-length of the rays to the path-length after reflection. In the usual arrangement spots of the second kind are about twice as far apart as spots of the first kind.

Duane's value for the wave-length difference of the $K\alpha$ doublet of molybdenum has been checked by measurements on spots of the first kind.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INC.
March 17, 1922.

Facts About Asbestos. (*Engineering World*, June, 1922, p. 371.)—The art of weaving the mineral fibre in asbestos, which is ordinarily indestructible, was rediscovered at a comparatively late period of civilization. Woven asbestos was used in the ancient pyre to preserve the royal ashes. Charlemagne is said to have had a table-cloth made of asbestos and to have cleaned it by throwing it into the fire, which consumed the dirt, thus illustrating in a spectacular manner one of the most valuable properties of this material.

The fibre of the best grade of asbestos is beautiful and silky and has great flexibility, elasticity and tensile strength. It can be spun into thread so fine as to run 225 yards to the ounce, and as it is incombustible as well as a non-conductor of heat and electricity and resists the action of most ordinary acids, its field of use is large. The possible applications of asbestos are far from fully appreciated, not only by the general public but by manufacturers who are in search of material for special uses to which asbestos may well be applied. Perhaps it is most generally used to make fireproof cloth for theatre curtains. It has been used also for making firemen's clothing. Everywhere in cold countries it is extensively employed for covering furnaces, boilers and pipes to prevent loss of heat. Asbestos is a good insulator. R.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THERMAL EXPANSION OF A FEW STEELS.[1]

By Wilmer Souder and Peter Hidnert.

[ABSTRACT.]

THERMAL expansion data on 28 samples of iron and steel are given. One sample of vacuum electrolytic iron and one of gray cast-iron are included. A specimen of hardened steel has been tested to show the dimensional changes incident to heat treatment or drawing. Twenty-two curves and a two-page table are used to summarize the results.

The average expansion of the specimen of electrolytic iron is 12.0×10^{-6} for the range 25 to 100° C.

For 25 steels:

11.2×10^{-6} for the range 25 to 100° C.

and 14.2×10^{-6} for the range 25 to 600° C.

Above the critical region the values usually jump to approximately 23×10^{-6}.

The values on cooling are not very different from those on heating; the transformation regions are displaced as usual.

The contraction and expansion reversals within the critical regions vary from a few microns per metre, if any at all, for a 3.7 per cent. silicon steel, to almost 2000 microns per metre for a 1.2 per cent. chrome steel (C, 0.35; Cr., 1.17; V, 0.14).

The critical region was found to extend over a temperature interval of from less than 6° C. for electrolytic iron to something over 100° C. for a special 1.1 per cent. manganese steel. These differences in dimensional changes and extent of critical region are suggested as a means for determining the tendency toward cracking or warping when parts of specimens are quenched at unequal rates. This rate is always different, depending upon the size, shape, etc.

The completion of the transformations on heating and the beginning on cooling were found to be separated by varying amounts, from 10 to 100° C., approximately. Since quenching

* Communicated by the Director.

[1] Scientific Papers No. 433.

temperatures are usually determined from heating curves rather than cooling curves, the question is raised as to the possibility of errors approaching 100° C. in these quenching temperatures.

The length changes of a piece of hardened steel indicate a small shrinkage when heated above 50° C. This continues for temperatures up to 100° C. After a repeated heating to 100° C. and holding at this temperature for a few hours no further shrinkage was observed, even upon carrying the temperature to 200° C. Upon heating to 250° C. a second shrinkage began and continued to approximately 375° C.

The specimen of cast-iron showed irregularities and considerable permanent growth upon heating, the growth being especially rapid at temperatures above 650° C.

A brief review of some of the previous work on expansion is included.

METALLOGRAPHIC ETCHING REAGENTS; II, FOR COPPER ALLOYS, NICKEL, AND THE ALPHA ALLOYS OF NICKEL.[2]

By H. S. Rawdor and Marjorie G. Lorentz.

[ABSTRACT.]

THIS article constitutes the second part of the general investigation of metallographic etching reagents in progress at this Bureau. It is closely related to the one already published on copper in the methods employed and results obtained. The following materials were used: Copper alloys, including brasses, bronze and aluminum bronze; nickel and the α alloys of nickel, monel metal, cupro-nickel and nickel brass.

Experimental results are given to show the importance of films in producing contrast in etching. Oxide and sulphide films were used, and it was shown by separating the etching and the filming operations that films varying in thickness on the individual crystals are produced by certain reagents and give rise to "contrast." The better understood method for producing contrast by a differential roughening of the crystals upon etching is also illustrated.

The α copper alloys closely resemble copper in their general behavior upon etching and in the character of the results produced. The addition of tin to brass appears to render it slightly less respon-

[2] Scientific Papers No. 435.

sive to etching reagents than the same alloy without tin; aluminum bronze in the rolled condition was the most unsatisfactory of the copper alloys examined to etch. A series of copper-zinc alloys representative of all the types of structure in this series was examined. The alloys rich in zinc resemble this metal in their etching characteristics more than they do the copper-rich alloys, in that highly oxidizing etching reagents do not appear to be necessary for the successful etching of the alloy.

Nickel, particularly when of high purity, is etched with considerable difficulty. Oxidizing acids, such as nitric, and acids to which strong oxidizers had been added were found effective for a quick etching. For producing a contrast etch-pattern with freedom from pitting a long immersion in concentrated hydrochloric acid was found to give excellent results.

Of the α nickel alloys examined, monel metal and cupro-nickel were found to resemble nickel in their etching properties, though they etched more readily. The nickel brasses (nickel silver) resemble the α copper alloys in many respects and were readily etched by the reagents used for the brasses and bronzes.

The copper alloys behave very similarly to copper in their behavior toward etching reagents through which oxygen was bubbled. They were readily etched by reagents, ammoniacal, acid, or neutral, which otherwise would have but slight effect upon them, provided a stream of oxygen was passed through the solution while the specimen was immersed. Nickel was found not to be effected materially in its rate of etching by the use of oxygen gas except in the degree of pitting produced in some specimens. Cupro-nickel and monel metal resemble nickel in this respect, and the nickel brasses are somewhat like the copper alloys. They respond to the ammoniacal solutions containing oxygen though not to acid solutions and oxygen.

THE SOLUBILITY OF DEXTROSE IN WATER.[3]

By Richard F. Jackson and Clara Gillis Silsbee.

[ABSTRACT.]

THE solubilities of dextrose, which are of fundamental importance in controlling the process of manufacture, have been determined over a range of temperatures extending to 90° C. The

[3] Scientific Papers No. 437.

respective solid phases were agitated in contact with their aqueous solutions in containers under the water of a thermostat until saturation was attained. The viscous saturated solution was separated from the crystals by an asbestos pressure filter constructed for the purpose. Solutions were analyzed by densimetric and polarimetric measurements.

Three solid phases are capable of existence below 90° C., namely, ice, α-dextrose monohydrate, and anhydrous α-dextrose. The freezing point curve, computed from existing data, intersects the solubility curve of dextrose hydrate at −5.3° C. and at a concentration of 31.75 per cent. dextrose. This intersection is therefore the cryohydric point.

α-dextrose with one molecule of water of crystallization is the stable phase between −5.3° C. and 50° C. It occurs in the form of minute lustrous plates which under carefully regulated conditions are capable of growth to six or more mm. in length. The solubility shows a very high temperature coefficient. Thus at 0.5° C., 100 g. of water dissolve 54.32 g.; at 30° C., 120.5 g.; and at 50° C., 243.8 g. of dextrose (calculated as anhydrous sugar).

The hydrate shows a melting point of about 83° C., the exact temperature being apparently uncertain and unreproducible. The solubility curve, however, can not by any manner of extrapolation be made to pass through this temperature at a concentration of 90.9 per cent. (the composition of the crystals). The solubility measurements were, however, shown to be compatible with the observed melting point on the theory that β-dextrose is present in the saturated solution, but absent during a melting point determination. By an approximate calculation of the solubilities of α-dextrose in solutions containing only α-dextrose, a solubility curve was obtained which was consistent with the observed melting point of the crystals.

The transition from α-dextrose hydrate to the anhydrous form occurs at 50° C.

Above the transition point the anhydrous form is stable and its solubility rises linearly, but with relatively small temperature coefficient. At 50° C. the solubility is 70.91 per cent.; at 70.2° C., 78.23 per cent.; and at 90.8° C., 84.9 per cent. The anhydrous form is capable of existing in metastable equilibrium below the transition point. It was found to be feasible to make approximate solubility measurements down to 28° C.

SENSITOMETRY OF PHOTOGRAPHIC EMULSIONS AND A A SURVEY OF THE CHARACTERISTICS OF PLATES AND FILMS OF AMERICAN MANUFACTURE.[1]

By Raymond Davis and F. M. Walters, Jr.

[ABSTRACT.]

THIS article is the result of a survey of about 90 different brands of photographic plates. In this survey the speed, developing characteristics, color sensitiveness, filter factors, and scale of the plates were investigated.

The introductory part deals in a general way with: The preparation and classification of emulsions; photographic filters: the relation between exposure of the photographic plate and the resulting density; the effect of time of development on contrast; speed and inertia; scale and latitude; other methods of measuring plate speeds; effect of the presence of bromide in the emulsion; and the general methods of development in use.

The second part is devoted to the apparatus and methods employed in the investigation. For obtaining the exposure density curves as well as the color sensitiveness of the emulsions a light source having both standard intensity and standard composition is necessary. For this the Bureau has chosen one having the composition of average noon sunlight at Washington and an intensity at the test plate of one candle metre—a Mazda C automobile headlight, operating on approximately 2.4 amps., combined with a suitable filtering screen.

The sensitometer, special design, was of the sector-disc type, exposing each of nine successive areas on a given plate, for double the time of the preceding area. With an ideal emulsion the brightness of a given field of light viewed through these different areas of the developed plate would be reduced by equal steps, passing from the area of least to that of greatest exposure. The instrument is described in Patent No. 1,382,272, R. Davis, sensitometer for testing plates and films—dedicated to the public. The exposures chosen were such that false values introduced by the intermittency of the light were negligible. For measuring the densities of the exposed plates a Martens photometer mounted in a specially designed illumination box was used. The plates were developed in silver-plated cans immersed in a thermostated bath.

[1] Scientific Papers, No. 439.

For investigating the color sensitivity two methods were employed: That of photographing the spectrum to reveal the region of sensitiveness; and that of measuring the filter factors to determine how one plate compares with another when different filters are used. For obtaining the spectrograms, a transmission diffraction grating was used, giving a normal spectrum, the red part of which passed through a yellow screen to cut out the violet rays of the next higher order. Between the source, giving uniform illumination of the slit, and the slit, a rotating sector was interposed which produced a geometrically decreasing illumination from bottom to top of the resulting spectrum. The rectangular area which the spectrum covers on the photographic plate shows, when the exposed plate has been developed, a dark peak wherever the plate is sensitive to the corresponding color. The results being qualitative rather than quantitative the source of light—a tungsten filament—was not adjusted to the composition of sunlight.

The filter factor apparatus was designed to reduce the intensity of the undimmed white light on the plate by a measurable amount until it gives, for the same exposure time, the same darkening effect as the light which passes through the filter. The ratio of the intensity used on the filter side to that used on the undimmed side is the filter factor of the given plate for the given filter. For this work, to give filter factors for outdoor purposes, a corrected source similar to that used with the sensitometer was employed. The reliability of the filter factors thus obtained is illustrated by comparative photographs.

The third part gives data obtained from practically all brands of emulsions made in the United States—the trade names of the emulsions being omitted.

THE REDWOOD VISCOSIMETER.[5]

By Winslow H. Herschel.

[ABSTRACT.]

THE Redwood viscosimeter was selected for calibration because it is standard in England and because there appeared to be some doubt as to whether or not the instrumental constants varied with the temperature. It is stated that the instrument is so adjusted that the time of flow for 50 cubic centimetres of rape seed oil at

[5] Technologic Papers No. 210.

60° F. (15.6° C.) is 535 seconds, but this oil is so variable in viscosity that the statement is of little value in determining the equation of the instrument. The standard dimensions are also inadequate as published.

By calibration with oils whose viscosity had been determined in a capillary tube instrument, the equation was obtained

$$\text{kinematic viscosity} = .00260\,t - \frac{1.88}{t}$$

where t is the time of flow in seconds.

In the course of the work two common errors in viscosimetry were investigated with the following results:

1. It was found that the error due to inaccuracy in the Meissner formula for average head was negligible in ordinary work.

2. The error due to cooling of the oil after leaving the outlet tube may be neglected at low temperatures, but should be corrected at temperatures near the boiling point of water. Diagrams were prepared to assist in making this correction.

The tests showed that any variation in instrumental constants at different temperatures is probably due to the last mentioned error, so that viscosimeters may be calibrated at any convenient temperature, varying the viscosity either by change of temperature or by blending. Outlet tubes may be made of any suitable durable and non-corrosive material, without regard to its coefficient of expansion. Thus the time ratios of the Redwood, Saybolt Universal, and Engler viscosimeters were found to be independent of temperature, although the outlet tubes of instruments of the first type are made of agate, and tubes of the other instruments are made of metal.

RADIATORS FOR AIRCRAFT ENGINES.[6]

By S. R. Parsons and D. R. Harper, 3rd.

[ABSTRACT.]

IN a technological paper bearing the above title, the National Bureau of Standards communicates much material which it is hoped will prove of value to the automotive industry, as well as of interest to physicists and engineers generally. The paper describes the laboratory investigations relating to aircraft engine radiators which were conducted by the Bureau of Standards during the

[6] Technologic Paper No. 211.

World War and in the two years immediately succeeding it. Individual reports covering many phases of the subject have been published previously in the technical series of the National Advisory Committee for Aeronautics and in scientific and engineering journals. These reports, however, lack the systematic coördination, uniform terminology, and unified mathematical treatment which should characterize a handbook on the subject. Moreover, the problems, which were investigated first because of their greater importance and which were the subjects of the reports published earliest, are for that reason not so well covered as is now possible because the later work threw much additional light upon matters not settled up to the time of publication of the early reports. Accordingly, the present paper is much more than a reprint of earlier reports, being a complete revision and recompilation of the material available.

The special investigations reported included development of the methods of measuring air flow in radiator tubes; experiments upon the effect of nature of surface upon air flow and upon heat dissipation from the surface of metal tubes to a high velocity air stream; experiments to ascertain the degree of turbulence in the air tubes of a radiator core; mapping of temperature distribution, axially and transversely, in the air tubes of radiator cores. In addition to recording these special investigations the paper contains a full description of laboratory methods and instruments for those tests of radiator cores properly made in the laboratory, both of physical properties and geometrical characteristics such as size and shape of air tubes and of water tubes.

The work included laboratory measurements of cooling power, head resistance, and geometrical characteristics of over one hundred types of radiator core. Performance characteristics of 66 types of core are given in graphical form. General conclusions from these measurements and from the special laboratory experiments mentioned above are incorporated into an exposition of the fundamental relations between the conditions under which a radiator operates, its characteristics of form and construction, and the properties which describe its performance. This portion of the designer's field is by no means the whole, however, and the paper does not treat the important consideration of sturdiness, ease of construction and repair, cost, form of design imposed by the structure of the aircraft, etc.

Among the features of the paper may be mentioned empirical

equations for relating heat dissipating power of a radiator to the air flow through the core, for computing the performance of a core of any depth from that of a core of exactly similar construction but different depth, for computing air flow through simple honeycomb cores for given flying speeds in an unobstructed position, and for computing heat dissipating power of such cores from their geometrical dimensions. The effectiveness of indirect cooling surface (cooling surface not backed by flowing water) is developed mathematically, reduced to a practical working equation, and applied to computation of optimum fin dimensions for given conditions. Also the equations of thermal conductivity are applied to produce a table showing temperature drop through metallic water tube walls of radiators of various wall thicknesses and material.

The effect upon heat dissipation of varying rate of water flow is considered in detail, also a comparison of methods of testing radiator cores calorimetrically, using superheated steam as a source of heat and using hot water as the source, a table being given which contains the essential steam data for computing results of a measurement made by the method first mentioned.

Many topics, treated briefly, have to do with such details of radiator performance as effect of yaw, slipstream mountings, wing radiators, shuttering, radiator requirements at altitude, and methods of computing performance at altitude from test data obtained under ground-level conditions. Experiments are described which investigated the effects of a partially streamlined casing enclosing a radiator. Experimental work upon a model fuselage nose radiator mounting showed clearly that for high speed flight the figure of merit of an unobstructed radiator and streamline nose is sufficiently above that of a nose installation to warrant careful study of the structural difficulties to be overcome in adopting such an arrangement.

TESTS OF STELLAR RADIOMETERS AND MEASURMENTS OF THE ENERGY DISTRIBUTION IN THE SPECTRA OF SIXTEEN STARS.[1]

By W. W. Coblentz.

[ABSTRACT.]

THE object of the present investigation was (1) to test new stellar thermocouples, (2) to verify previous measurements of

[1] Scientific Papers No. 438.

stellar radiation, (3) to measure the radiation intensities of bright stars in the region of 0 hours to 12 hours, in right ascension, not previously measured, and (4) to determine the feasibility of the method of obtaining the spectral energy distribution of stars by means of transmission screens which, either singly or in combination, are placed in front of the vacuum thermocouple.

By means of vacuum thermocouples, measurements were made on the total radiation intensities of thirteen bright stars not observed in 1914, thus completing the survey of the whole sky. A total of thirty celestrial objects were measured, including Venus and Mars.

By means of a series of transmission screens (of yellow and red glass, of water, and of a thick plate of quartz) wide spectral regions were isolated and the radiation intensities in the spectrum from 0.3μ to 0.43μ, 0.43μ to 0.6μ, 0.6μ to 1.4μ, 1.4μ to 4.1μ, and 4.1μ to 10μ were determined. In this manner the distribution of energy in the spectra of sixteen stars was determined, thus obtaining for the first time an insight into the radiation intensities in the complete spectrum of a star.

By means of these transmission screens it was found that in the Class B and A stars the maximum radiation intensity lies in the ultra-violet (0.3μ to 0.4μ) while in the cooler (Class K and M) stars the maximum emission lies at 0.7μ to 0.9μ in the infra-red.

A calculation is made of the spectral component radiations of a black body at various temperatures, using the spectral transmission data on these screens. From a comparison of the observed and the calculated spectral radiation components, it appears that the black body temperature (that is, the temperature which a black body would have to attain in order to emit a similar relative spectral energy distribution) varies from 3000° K. for red, Class M, through 6000° K. for the yellow, solar type stars to 10,000° K. or perhaps even higher for blue, Class B, stars.

The observing station being much higher (7300 feet as compared with 4000 feet) than previously used, the atmospheric scattering of light was greatly reduced, and consequently the transmissions of the violet are somewhat higher than previously observed when the water cell was interposed. However, all the data verify previous measurements showing that red stars emit three to four times as much infra-red radiation as blue stars of the same visual magnitude. Moreover, observations made on the

same night (same weather conditions) are consistent in showing small gradations in the infra-red radiation components, corresponding with the small gradations (say B2 and B8) in spectral types.

For binary stars having companions of low luminosity the water-cell transmissions are low, indicating that the companion stars emit considerable infra-red radiation.

Among the subsidiary investigations made with a view to the improvement of stellar radiometers, this paper gives data on the radiation sensitivity of thermocouples of alloys of gold-palladium, platinum-rhodium, bismuth-tin, bismuth-antimony, and also of pure bismuth.

CARBON MONOXIDE IN PRODUCTS OF COMBUSTION FROM NATURAL GAS BURNERS.[8]

By I. V. Brumbaugh and G. W. Jones.

[ABSTRACT.]

CARBON MONOXIDE, a very poisonous gas, is produced in combustion processes where there is a deficiency of oxygen for completely burning the carbon in the gas to carbon dioxide. Conditions favorable for the production of carbon monoxide result with the usual type of gas burner when the flame is insufficiently aerated. It occurs if the burner is placed too close to the utensil.

Carbon monoxide combines with the hemoglobin of the blood and temporarily destroys its function as an oxygen carrier. The affinity of carbon monoxide for hemoglobin is 250 to 300 times as great as oxygen, and it is easily seen why a small percentage of carbon monoxide soon becomes very dangerous to health when inhaled for some time. The maximum percentage of carbon monoxide allowable for continuous exposure from a hygienic standpoint should not be greater than 0.02 per cent., and for intermittent exposures of 1 hour, not greater than 0.04 per cent.

It is known that the efficiency of natural gas burners can be greatly increased by placing the burner close to the utensil. It is, therefore, very important to know how close the burner can be placed to the utensil without producing dangerous quantities of carbon monoxide. In this connection it is necessary to make a study of the effect of different types of flames on the production

[8] Technologic Papers No. 212.

of carbon monoxide. Different types of flames are obtained by changing the position of the air shutter so as to change the amount of primary air injected into the burner with the gas.

Tests for carbon monoxide were made with top burners of standard size at rates of consumption of 6.0 and 8.0 cubic feet per hour (6480 and 8640 Btu per hour). From the many tests made under a variety of conditions the maximum quantity of carbon monoxide was found to be 0.25 cubic foot per hour. Taking for comparison a room of 1000 cubic feet capacity, which can be considered as representative of the size of the average kitchen, and taking 0.04 per cent. of the maximum limit of carbon monoxide permissible for healthful conditions for 1 hour's exposure, it would take over 1½ hours before the concentration reached 0.04 per cent. if only one burner was operated and the room was unventilated. If as many as four burners were used under the same condition at one time, the carbon monoxide would have increased to 0.04 per cent. in less than half an hour.

It was observed that no carbon monoxide was found where the distance of the utensil from the burner was such that the blue inner cone of the flame did not touch the utensil.

For the same rate of consumption and the same ratio of primary air to gas one design of burner may permit the utensil to be placed as close as ¾ inch, while another design may require a distance of more than 1¼ inches in order that the amount of carbon monoxide be negligible.

For a given air shutter setting which determines the ratio of primary air to gas, the highest percentages of carbon monoxide are produced when the utensil is placed so close to the burner as to cause a "floating flame." When using the same burner with the utensil at a position that causes the flame to float, the carbon monoxide increases as the primary air rate is decreased. Therefore, a yellow flame will produce carbon monoxide at a rate greater than a blue flame.

Much of the carbon monoxide is surely produced by the smothering of the flame with the products of combustion, which are hindered in their escape at the close positions of utensil from burner by the unavoidable baffling of the supply of secondary air. It is generally reported that carbon monoxide is produced by the chilling of the flame with a relatively cold surface.

Ventilation is essential where gas is consumed. Normal air

contains 20.9 per cent. of oxygen. A natural gas flame was found to be smothered from deficiency of oxygen when the content of the atmosphere had been diminished to about 15.5 per cent. A very dangerous amount of carbon monoxide was found to be present at the condition where the flame was smothered out.

Under the worst conditions of top burner operation the amount of carbon monoxide liberated by the five different burners tested was not enough to be dangerous to health unless one worked directly over the burner or several burners were in use at the same time for several hours, or the room was unventilated.

When one considers the natural ventilation which takes place through the windows and doors it would seem that the danger from carbon monoxide poisoning with natural gas top burners is quite remote.

Leather and Humidity. (*U. S. Department of Agriculture, Press Service Sheet No. 205.*)—The strength and elasticity of leather are greater when the air is moist than when it is dry, and for this reason, says the Bureau of Chemistry, it is important in making comparative tests of leather to be sure that all pieces tested are under the same humidity conditions. A good piece of leather tested in a dry atmosphere might appear to be weaker than a much poorer piece tested when the air was moist.

Tests made of more than 500 pieces taken from the most uniform part of the hide, alternate strips being subjected to dry air and damp air at a temperature of 70° F., showed that an increase from 35 per cent. relative humidity to 55 per cent. increased the strength of the leather 13 per cent. and the stretch 16 per cent. When the humidity was raised from 35 per cent. to 75 per cent. the average increase in strength was 42 per cent. and in stretch 53 per cent.

It is apparent that control of the humidity in a room where leather is tested is necessary if the results are to be worth anything. The Bureau of Chemistry has devised such a room in which the amount of moisture in the air may be kept uniform and at any percentage of saturation continuously. It is the only testing room in the world where the conditions are controlled so well.

The United States spent $600,000,000 for roads in 1921, according to estimates of the Bureau of Public Roads, United States Department of Agriculture. This sum was derived from the following sources: Local road bonds, 33 per cent.; county, township, and district taxes, assessments, and appropriations, 14 per cent.; state taxes and appropriations, 12 per cent.; state road bonds, 7 per cent.; motor vehicle license revenues, 19 per cent.; Federal aid, 14 per cent.; and miscellaneous sources, 1 per cent.

On Atoms and Molecules. ALBERT C. CREHORE. (*Phil. Mag.*, May, 1922.)—It must not be supposed that the regnant Rutherford atom alone is being considered. In this article you will find a photograph of models of the lighter elements and of their isotopes, wherein there is a far departure from the arrangement of a positively charged nucleus with its satellites of electrons.

G. F. S.

On the Molecular Scattering of Light in Water and the Color of the Sea. C. V. RAMAN. (*Proc. Royal Soc.*, A 708.)—"The theory that the light of the sky owes its origin and colour to diffraction by the molecules of the atmosphere is now established on a firm experimental basis by the brilliant work of Cabannes and of Lord Rayleigh on the scattering of light by dust-free gases, and by the measurements of the transparency of the higher levels of the atmosphere in the visual region of the spectrum, which have yielded results in close agreement with the calculated values. It is the purpose of the present paper to point out the part played by molecular diffraction in another of the great natural optical phenomena, that is, the colour exhibited by large masses of clear water when illumined by sunshine and viewed from above, the depth being so great as to provide a perfectly black background for observation."

The "theory of fluctuations," developed by Einstein and Smoluchowski, is applied to the problem and a formula is obtained in which the outstanding relation is this. When a beam of light is traversing a body of water the intensity of the light diffused perpendicularly to the direction of the ray is inversely proportional to the fourth power of the wave-length of the light. "Volume for volume, water at 30° should scatter light 159 times as strongly as dust-free air under standard conditions." The result of the operation of the inverse fourth power law is that the shorter wave-lengths, the blue and violet, are diffused laterally to a much greater extent than the long reds and yellows.

The author combats Lord Rayleigh's view that the blue of the sea is due to reflected skylight. "Light reflected at the polarising angle from the surface of a liquid may be quenched by observation through a suitably oriented nicol. Hence by observing a tolerably smooth patch of water through a nicol at the polarising angle, the surface reflection may be got rid of. During a recent voyage, the writer made some observations by this method in the deeper waters of the Mediterranean and Red Seas, and found that the colour of the sea, so far from being extinguished when the sky-reflection is cut off is seen with wonderfully improved vividness and with saturated hues."

The entire trend of this paper is in opposition to the opinion that the color of large masses of water is due either to absorption or to reflection or to the presence of suspended matter. The scattering of the light is ascribed to the molecules of water.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

NOTE ON PROFESSOR SVEDBERG'S METHOD OF GRAIN ANALYSIS OF PHOTOGRAPHIC EMULSIONS.[1]

By S. E. Sheppard and A. P. H. Trivelli.

[ABSTRACT.]

F. F. RENWICK has suggested that the method of Svedberg may have left grains incompletely developed. On removing the developed grains and measuring, the partly removed grains would be measured as whole grains with smaller dimensions. The authors have investigated this by removing the developed grains with pure chromic acid which left a ghost of the grain composed of red silver chromate together with oxides of chromium. The photomicrograph then showed a sharp distinction between the developed and undeveloped grain. It was found in the case of two minutes' development with pyro that the grains develop completely so that Svedberg's method is a valuable and reliable method of optical analysis.

Burning of One Hundred Tons of Picric Acid.—Picric acid was packed in barrels, each containing approximately 400 pounds of the acid. An open shed magazine contained 500 barrels of the acid. Red hot carbon, forced from the exhaust of a tractor ignited, exposed picric acid which had sifted from the barrels. The entire 100 tons of picric acid were consumed in the resulting fire. The flames reached a height of 35 to 40 feet, and had a reddish color. The heat was so intense that the metal in the roof and in the barrel hoops was melted, and a portion of it was completely burned. Abundant heavy black smoke was noted during the early stage of the fire; however, combustion of the carbon became more complete as the temperature increased (CHARLES E. MONROE, *Jour. Ind. Eng. Chem.*, 1922, xiv, 552–554).

J. S. H.

* Communicated by the Director.

[1] Communication No. 137 from the Research Laboratory, Eastman Kodak Company, and published in *Phot. J.*, (London) April, 1922, p. 196.

On Seeing Ultramicroscopic Particles with the Naked Eye. J. TRAUBE and P. KLEIN. (*Physik. Z.*, April 15, 1922.)—When a beam of light passes through an optically empty liquid, its path there is invisible, though the places of entrance and of exit may be seen. In a colloidal solution, on the other hand, the path appears as a uniformly illuminated cloudy space. If any particle can be seen by itself, by the naked eye, within this space, it must be large enough to be seen in like manner elsewhere. The authors happened to notice that the addition of sodium carbonate to a solution of lead nitrate gave rise to a cloud space along the path of the light in which individual particles could be seen. The result was obtained upon adding two drops of a one-half normal sodium carbonate solution to 30 c.c. of a one-thirty thousandth normal solution of lead nitrate. When the path of light was observed with a lens there was seen for somewhat less than a minute a swarm of particles in violent but irregular motion. A minute later the unaided eye at a distance of five metres could see the same thing.

This effect is similar to the Brownian Movements. The particles concerned are of extremely small dimensions. In one instance where the effect was well seen no inhomogeneity of the liquid could be seen under a microscope of high magnification.

The effect can be obtained only with solutions of certain concentrations, though a number of different solutions may be used. Siedentopf of Jena explains it as a diffraction phenomenon connected with tiny needle-like crystals.

G. F. S.

Contamination of Air with Carbon Monoxide.—YANDELL HENDERSON and HOWARD W. HAGGARD, of Yale University (*Jour. Ind. Eng. Chem.*, 1922, xiv, 229–236), draw the following conclusions from their experiments in which the period of exposure was several hours. The time of exposure in hours is multiplied by the concentration of the carbon monoxide in parts per 10,000 of air. If the product equal 3, no perceptible physiological effect is noted; if it equal 6, the effect is just perceptible; if it equal 9, headache and nausea are produced; if it equal or exceed 15, conditions are dangerous to life. Exercise and physical work increase the rate of absorption of carbon monoxide from a contaminated atmosphere. Upon return to fresh air, the carbon monoxide which has been absorbed by the blood, is excreted through the lungs; from 30 to 60 per cent. of the absorbed carbon monoxide is excreted hourly. Carbon monoxide is the only toxic constituent of importance in the exhaust gas from gasoline. Illuminating gas and the exhaust gas from coal tar distillate contain other toxic constituents as well as carbon monoxide.

J. S. H.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

SOME CHANGES IN THE COMPOSITION OF CALIFORNIA AVOCADOS DURING GROWTH.[1]

By C. G. Church and E. M. Chace.

[ABSTRACT.]

IF packed too early, the avocado has a tendency to shrivel and become "rubbery," is watery, and lacks the characteristic flavor of well-matured fruit. Thus its maturity problem is of special importance. The Bureau of Chemistry has recently completed an investigation on the composition of several varieties of the avocado at the various stages of its growth.

No satisfactory correlations between physical properties and maturity were found in the avocados examined.

The proportion of many of the constituents of the avocado changes during its development, the most marked change being the increase of the fat content. This takes place rapidly while the fruit is immature, and much more slowly as it approaches maturity, with possibly a slight decrease if the fruit remains too long upon the tree. It is accompanied by a decrease in sugar content.

Fruits rich in fat (above 20 per cent.) contain at least 70 per cent. of that constituent on a water-free basis at maturity.

On storage of immature fruits there is an apparent increase in the proportion of fat, accompanied by a decrease in the sugar content and undetermined matter.

Mature fruits on storage do not show this increase to the same extent, and at times show some loss.

No standards of maturity are recommended.

A COLOR TEST FOR "REMADE MILK AND CREAM."[2]

By O. L. Evenson.

[ABSTRACT.]

A PRACTICAL qualitative test for distinguishing natural pasteurized milk from a mixture of natural and remade milk has

* Communicated by the Chief of the Bureau.

[1] Issued as *U. S. Dept. Agr. Bul. 1073*, May, 1922.

[2] Published in *J. Dairy Sci.*, 5 (1922): 97.

been devised. This test is based upon the discovery that a yellow color is produced when the worked curd of milk made from milk powder is treated with sodium hydroxid. The color is probably due to the combination of a trace of lactose with the protein during the process of manufacturing the milk powder.

THE PROTEINS OF THE TOMATO SEED, SOLANUM ESCULENTUM.[2]

By C. O. Johns and C. E. F. Gersdorff.

[ABSTRACT.]

ANALYSES of five samples of tomato seed and press-cake show an average content of 36.91 per cent. of protein (N × 6.25). The total globulins were extracted from the press-cake by extraction with 0.5 per cent. sodium hydroxid. Preparations obtained from these extractions gave uniform results on analysis. From seed of high germinating quality two globulins, α and β, have been isolated and analyzed. These globulins, coagulable by heating for ten minutes at 74 and 96° C., are precipitated from their saline solutions by 0.3 of saturation, in the case of the α-globulin, and by saturation with ammonium sulphate, in the case of the β-globulin. They differ in their solubility, the α-globulin being easily denatured, while the β-compound is highly soluble in mere traces of aqueous sodium chloride.

The elementary analyses of the two globulins show the following percentage of differences in composition: The α-globulin contained carbon, 52.29, nitrogen, 18.34, and sulphur, 1.16; while the β-globulin contained carbon, 51.21, nitrogen, 16.02, and sulphur, 0.81. The sulphur content of the globulins is in the ratio of 3 : 2. The analyses by the Van Slyke method show that the nutritionally essential basic amino acids are well represented in these globulins.

It is of interest to note that these globulins are high in both arginine and lysine. The β-globulin contains also an unusually large proportion of histidine, while in the α-globulin the histidine content is low. Both globulins respond to the qualitative tests for tryptophane and tyrosine. In the distribution of the nitrogen based on the weight of the proteins, as calculated from the Van

[2] Published in *J. Biol. Chem.*, 51 (1922): 439.

Slyke analyses, the most marked difference is found in the figures for the non-basic nitrogen.

Tests failed to disclose the presence of albumin and glutelin.

A CHEMICAL STUDY OF THE PROTEINS OF THE ADSUKI BEAN, PHASEOLUS ANGULARIS.[4]

By D. B. Jones, A. J. Finks, and C. E. F. Gersdorff.

[ABSTRACT.]

THE adsuki bean contains about 21.13 per cent. of protein (N × 6.25), 16.7 per cent. of which is extracted by means of a 5 per cent. aqueous sodium chloride solution.

By fractional precipitation of the sodium chloride extracts with ammonium sulphate two globulins, designated as the α- and β-globulins, have been isolated. The former was precipitated by the addition of ammonium sulphate in sufficient amount to make the original extract 0.3 saturated. A small fraction consisting of a mixture of the two globulins was separated from the filtrate by increasing the concentration of ammonium sulphate up to 0.65 of saturation. This fraction was discarded, and the β-globulin was precipitated by making the solution completely saturated. A small quantity of an albumin was found in distilled water extracts of the bean, after the globulins had been removed.

The two globulins differ markedly in their sulphur and nitrogen content and in their nitrogen distribution, as determined by the method of Van Slyke.

Proper Use of Coal.—Bulletin No. 9, just issued by the Department of Internal Affairs of Pennsylvania, contains a paper by G. H. Ashley, State Geologist, advocating strongly a more economical use of coal, especially the coking-coals of the State.

The high volatile coals of Pennsylvania can be made to yield from four to six times the quantity of oil now being obtained from the State wells. In view of this, we are surely not justified in burning raw soft coal for raising steam when the yield of hydrocarbons is thus diminished. One authority, perhaps a little enthusiastic, has declared that within a few years it will be against the law to burn such coal. This is a desirable result, but it may not be very near at hand. Pennsylvania coking-coals were used for over eighty years in beehive ovens, but all the gaseous products were lost. It is not merely the tar and volatile hydrocarbons that are thus destroyed;

[4] Published in *J. Biol. Chem.*, 51 (1922): 103.

a considerable amount of ammonia is wasted. The value of ammonia in modern industries is now recognized, especially when we recall the vast amount of money and scientific investigation which Germany lavished on the synthetic ammonia process. Our ordinary methods of steam-making are wasteful of fuel as such, apart from the attendant objection from smoke. Greater efficiency has been obtained of late years, but even with the best conditions the results are not comparable to those obtained with liquid fuels in internal combustion engines.

The increasing use of gasolin and the rapid depletion of the oil reserves of the United States and Mexico will compel searches for other sources of liquid fuel. Two such sources are now attracting much attention, the oil-shales and coal. Exploitation of the former is still in the experimental stage, but the distillation of coal is, in the main, a solved problem. By-product coke ovens are often operated at a rather high temperature. A slightly larger yield of coke can be obtained from the by-product oven than from the beehive form. Coke is a smokeless fuel, very much of the type of anthracite, but not nearly so compact and, therefore, burning more rapidly. The use of coke in domestic heating in the winter would be satisfactory along all lines except that a greater storage capacity would be needed and visits to the furnace would be somewhat more frequent. The proportion of light and heavy oil and of gas obtained from a given coal can be modified by the temperature, and experiments on the low temperature distillation are reaching the stage of commercial production in England, Germany and the United States. One ton of Kentucky coal containing 3 per cent. of moisture, 35 per cent. volatile matter, 55 per cent. fixed carbon and 7 per cent. ash, is said to yield 1400 pounds of carbocoal, 30 gallons of tar, 9000 cubic feet of gas, 20 pounds of ammonium sulphate, and 2 gallons of light oil thrown down from the gas.

The term "carbocoal" refers to a product obtained in Virginia by a special process of distillation. It is softer than ordinary coke and contains from 8 to 10 per cent. of volatile matter. It could be used at the point of production, but is said to be not suited to the general market. It is, however, employed in the manufacture of briquets, which are stated to be of good quality.

The tar contains no naphthalene but is rich in tar-acids and cresols, and contains more phenol than in other forms of tar. So far as Pennsylvania coal is concerned, it has been estimated from the results obtained in England, that by carbonizing the 140,000,000 tons of bituminous coal now mined in Pennsylvania, in a year, more than 400,000,000 gallons of motor fuel and one billion and a quarter gallons of Diesel and lubricating oils could be obtained. The total of these figures is about five times the quantity of oil now being produced in Pennsylvania. In addition over a million tons of ammonium sulphate would be obtained and the fixed residue, amounting to over a hundred million tons, would be an excellent smokeless fuel. H. L.

NOTES FROM THE U. S. BUREAU OF MINES.*

SEPARATION OF PALLADIUM AND PLATINUM.

By C. W. Davis.

In the investigation of methods for assaying platinum conducted by the Bureau of Mines, recent experiments have developed that with certain ores, especially when the quantity of platinum is considerable, nitric acid will not effect a separation of platinum and palladium.

Wunder and Thuringer [1] have developed methods for the separation of palladium from all the platinum metals except platinum by means of dimethylglyoxime. All of their precipitations were carried out while the solutions were being heated. This caused a partial precipitation of the platinum along with the palladium.

A few preliminary tests substantiated the belief that palladium could be precipitated free from platinum if a solution of the chlorides of these metals be treated at room temperature with an alcoholic solution of dimethylglyoxime. The following procedure was worked out to separate and determine platinum and palladium quantitatively.

The platinum and palladium free from the other platinum metals are obtained by the method given in U. S. Bureau of Mines Technical Paper 270. These metals are ignited and cooled in an atmosphere of hydrogen and weighed together. The weighed metals are dissolved in a little aqua regia and evaporated just to dryness. The residue is moistened with a drop of hydrochloric acid and after the addition of a little distilled water, a solution of dimethylglyoxime is added, drop by drop, with constant stirring until there is no further precipitation. After standing at room temperature for a few minutes the voluminous yellow precipitate is filtered off, washed thoroughly with distilled water and ignited slowly and carefully, first in air to drive off organic matter and then in hydrogen to reduce any oxidized palladium to the metal. The metallic palladium is then weighed.

* Communicated by the Director.

[1] *Comp. rend*, t. 30, 1913, p. 12.

The platinum may be found by difference or it may be recovered and weighed. To recover the platinum the filtrates from the palladium precipitation are carefully evaporated to dryness in a small pyrex beaker or porcelain dish, a little nitric acid being added as the volume becomes small. The residue is heated almost to redness to drive off all organic matter, the presence of which would prevent the complete precipitation of platinum. The residue is extracted with a little aqua regia, is evaporated just to dryness, is extracted with a drop of hydrochloric acid, and is diluted with a little distilled water. The solution is made alkaline with sodium carbonate, acidified with an excess of formic acid, and boiled to precipitate the platinum, which is filtered off, washed, ignited, and weighed. Further details are given in a recent publication of the Bureau.

THE SULPHUR DIOXIDE LEACHING PROCESS.

By Charles E. van Barneveld.

THE sulphur dioxide leaching process, developed at the Southwest experiment station of the U. S. Bureau of Mines, Tucson, Arizona, was devised to provide a cheap and efficient method for treating the so-called "porphyry" copper ores of the Southwest which generally contain both "sulphide" and "non-sulphide" copper minerals, mixed in such proportions that they can only be satisfactorily treated by a method which will concurrently recover both the sulphide copper and the non-sulphide copper. The latter term has been adopted to include all the minerals commonly referred to in operating phraseology in the mills of the Southwest as "oxidized," "oxide," or "soluble" copper. The process was developed with the coöperation of the Miami Copper Company and the Arizona Copper Company, and is suitable and commercially available for a wide range of ores.

While the process is called an SO_2 leaching process, it is in no sense an offshoot or development of the early Neill-Burfeind "leaching" process or of later modifications thereof which involve the retention of all dissolved copper in solution as copper sulphite, a notoriously unstable compound, to be later precipitated as cuprocupric sulphite (Cu_2SO_3, $CuSO_3$). Instead, it is a continuous leaching process controlled to form solutions of copper sulphate direct from oxidized copper ore, ranging in fineness from 20 to 48

mesh, pulped with water containing the usual proportion of reclaimed mill liquid, treated counter-current with dilute SO_2 roaster gas containing a large excess of oxygen over the amount necessary to completely oxidize all sulphites formed. Thus all difficulties met with in the aforementioned processes from the formation of unstable complex copper salts are avoided. No attempt is made to regenerate the leaching solutions; the sulphur supplied finally goes to waste as sulphates of the acid-soluble constituents of the ore, and as iron sulphates formed during precipitation of dissolved copper on iron.

Sulphur dioxide made from any convenient source, such as native sulphur, massive pyrite, or concentrate carrying upwards of 20 per cent. sulphur, may be utilized. If smelter gases containing 2 per cent. SO_2 by volume are available, they may be utilized direct from the stack. The ordinary volatile impurities found in smelter gases, such as arsenic and antimony, are not detrimental in this application of SO_2 leaching. Further details are given in a report issued by the Bureau in mimeograph and in more complete form in Technical Paper 312, now in course of publication.

ACETYLENE NOT A PRECIPITANT FOR CYANIDE SOLUTIONS.

By John Gross.

In connection with some investigations being made by the Bureau of Mines, on the precipitation of gold and silver from cyanide solutions, it was suggested that the effect of acetylene for this purpose be investigated.

The acetylene used in the tests was from commercial calcium carbide. Experiments resulted in more or less complete precipitation of silver, but no gold.

As silver acetylene, obtained by precipitating the silver from an ammoniacal solution of silver nitrate by acetylene, is yellowish white, easily soluble in cyanide and highly explosive, and the precipitate obtained from the cyanide solutions was black, not soluble in cyanide and not explosive, it was decided to investigate the nature of the silver precipitate from the cyanide solutions. In preparing a large quantity of the precipitate it was found that after complete precipitation of the silver the solution contained

soluble sulphides. This provided a clew and after appropriate tests the precipitation was proved to be silver sulphide.

The conclusion drawn was that a small amount of hydrogen sulphide was contained in the acetylene and that this was the active precipitating agent. Other tests were made, all of which verified the conclusion that acetylene, free from hydrogen sulphide, had no precipitating power on cyanide solutions of silver or gold. Further details are given in a recent report issued by the Bureau.

A Photographic Spectrum of the Aurora of May 13-15, 1921, and Laboratory Studies in Connection with It. LORD RAYLEIGH. (*Proc. Royal Soc.*, A 709.)—A very good photograph of the spectrum was obtained on the night of May 14. On the plate there appears a trace of a continuous spectrum, to be attributed to moonlight, the negative nitrogen bands in the blue, the violet and the ultra-violet and yellow-green aurora line. Strangely enough the bands are stronger than the line. When the spectrum of krypton was photographed on the same plate its characteristic line appeared in "approximate coincidence" with the auroral line.

It was not found possible to reproduce in the laboratory the nitrogen bands as they manifested themselves in the light of the aurora. Through excitation of nitrogen by atomic rays a good imitation was got, but other spectra of the gas persisted in appearing under the conditions of experiment. The cathode ray spectrum in nitrogen was free from these spectral interlopers but the distribution of intensity among the bands was not the same as in the aurora.

"We have reason to believe, not indeed from direct experiment, but on very strong theoretical grounds, that the upper atmosphere, in which the aurora occurs, is rich in the lightest constituents of air, helium and (possibly) hydrogen. Do these constituents appear in the auroral spectrum? The photographs reproduced confirm clearly all previous evidence that they do not. We are faced, therefore, with the alternatives that either they are not there, or that the conditions of excitation are not such as to develop the spectrum. According to all laboratory experience, even a trace of hydrogen asserts itself in the spectrum of any kind of an electric discharge through air, under any conditions of pressure." The origin of the aurora is not definitely known. "There is a good deal of evidence from the work of Birkeland, Stormer, and Vegard, for attributing the aurora to cathode rays from the sun." An objection to this explanation is that, as stated above, in the laboratory cathode rays fail to give the desired distribution of intensity in the band spectrum of nitrogen. On other grounds the author finds it very difficult to account for the origin of the aurora on the basis of excitation by atomic rays, even though these in the laboratory do give the same intensity distribution as that in the auroral spectrum. G. F. S.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, June 7, 1922.)

HALL OF THE INSTITUTE,
PHILADELPHIA, June 7, 1922.

DR. JAMES BARNES *in the Chair.*

The following report was presented for final action:

No. 2784: Vaphor Phase Oxidation of Benzene to Maleic Acid. The Howard N. Potts Medal Jointly to Messrs. John Morris Weiss and Charles R. Downs, of New York.

The following reports were presented for first reading:

No. 2767: Audion.

No. 2790: Automatic Cashier.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTION TO MEMBERSHIP.

(Stated Meeting, Board of Managers, June 14, 1922.)

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NECROLOGY.

Mr. Charles A. Lindstrom, Pressed Steel Car Company, Pittsburgh, Pennsylvania.

Dr. Walter L. Pyle, 1931 Chestnut Street, Philadelphia, Pennsylvania.

LIBRARY NOTES.

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BOOK NOTICES.

CATALYTIC ACTION. By K. George Falk. Harriman Research Laboratory, Roosevelt Hospital, New York. 165 pages and index, 8vo. The Chemical Catalog Company, New York, 1922. $2.50 net.

In this compact and neatly printed volume the author has collected a large amount of information upon one of the most puzzling problems of chemistry. The terms "catalysis" and "catalytic" were introduced by Berzelius in 1836. A portion of Berzelius' essay, in which he discussed this class of phenomena and suggested the terms, is quoted in the introductory chapter and makes interesting reading. The reactions that he studies covered a large range, such as the transformation of starch under the influence of acids, the decomposition of hydrogen peroxide in alkaline solution by several substances, and the production of ether by the action of sulphuric acid on alcohol. It is worth noting that four years before Berzelius published the paper, Döbereiner had called attention to the remarkable power of a small amount of manganese dioxide to cause the decomposition of potassium chlorate at a low temperature, and that the manganese compound undergoes no appreciable change. Berzelius spoke of catalysis as a "new force," but stated that he did not regard it as wholly independent of electrochemical affinities, being, he thought, merely a new manifestation of the same, but provisionally designating it by a special term. He, of course, with the information then at hand, found catalytic action more often manifested in organic than in inorganic reactions, and suggested that many of the processes of living organisms were of this nature. We know now the wide influence that catalysis has in life processes, and also many instances in non-living matter. The author calls attention to the fact that in Berzelius' time the concepts of "force" and "chemical affinity" were not the same as those attached to these terms today, but the criteria, which the Swedish chemist applied to determine whether a given action is or is not catalytic, are essentially those now employed.

The book is devoted to the consideration of catalytic action from the point of view of modern physical chemistry. It is not a manual of practise, but of theory. The author is well known for his wide acquaintance with the field both in theory and practise, and has, in the present essay, devoted himself to the elucidation of the complex conditions manifested in catalytic actions, of which so many instances and such variety are now known. He lays especial stress on Ostwald's principle that a catalyst is essentially a substance that accelerates a reaction, rather than causes it. Presumably, by this is meant that a perfectly sterile solution of pure sucrose in pure water would in time be converted into invert sugar, but the introduction of a small amount of invertase brings about the change promptly.

It has long been known that catalysts, especially the organic forms, require specific conditions of temperature and reaction for their operation. The views concerning hydrogen-ion and hydroxyl-ion concentration have found important applications in this field. The total acidity or alkalinity, measured by ordinary titration, does not supply the data necessary to determine the true reaction of the liquid to the catalyst or to the other organic materials, living or non-living. Much information on this phase of the question is given in the book.

Distinction is made between catalysts formed by living cells and those not so formed. The familiar term "enzyme" is applied to the catalysts originating in living organisms. The great part that these play in the phenomena of growth and development of all forms of life has been long evident,

and research is constantly adding other instances. It is a question, however, whether there is any use in making this distinction. The word "catalyst," coined with the laudable intention of providing a term for an important class of phenomena, fell somewhat into disrepute, because often used as cover for ignorance, but it is now rescued from such condition, and may take its place among the reputable terms of science. An effort was made to set aside a termination as an indication of the catalytic function, namely, the use of the syllable "ase." Falk does not seem to be in sympathy with this for he speaks of "emulsin," "trypsin," etc. This is in accordance with the custom of many authors of chemical and physiological text-books, but it is to be regretted that the simple nomenclature has not been generally adopted. Falk does, however, use the termination in some cases, speaking of lipase, lactase and other similar substances. The spelling "sulfuric" and cognate forms, that has been a feature of the publications of the Chemical Catalog Company, is retained, but it is unfortunate that the other and even more useful reforms, suggested years ago by the Chemical section of the A. A. A. S., have not prevailed, and that American chemists, pharmacists and physiologists seem to have got cold feet on the issue of simplifying English spelling.

A special chapter is devoted to the "Chemical Interpretation of Life Processes." This is the most fascinating and important phase of human study, but while the chapter contains a large amount of information and shows a diligent and appreciative study of the literature, with ingenious interpretations of the phenomena, it does not seem that the secret of life is disclosed. The organic catalysts (enzymes, of our author) have some resemblances to living matter, and the present reviewer, many years ago, suggested that they may be considered as the connecting link between the non-living and living forms. They require certain conditions for actions and may be restrained by conditions that do not seem actually to destroy them.

The closing chapter, on "Contact Catalysis," presents an elaborate discussion of effects that have extensively applied in industrial chemistry, such as the action of platinum in the manufacture of sulphuric acid, and of some metals in the hydrogenation of oils. The latest developments of physical chemistry have been brought to bear in the elucidation of these phenomena. The work is a most valuable contribution to the literature of a subject that, in spite of the extensive investigation to which it has been subjected, seems yet but superficially developed. Each research but indicates more problems:

"Hills peep o'er hills, and Alps on Alps arise."

HENRY LEFFMANN.

THE OUTLINE OF SCIENCE. A Plain Story Simply Told. Edited by J. Arthur Thomson, M. A., Regius Professor of Natural History in the University of Aberdeen. 296-pages, 40 colored plates and 800 illustrations, 4to. In four volumes; volume one. G. P. Putnam's Sons, New York, 1922. Price $3.75 per volume.

"Boy, page Mr. Bryan." Surely the great American Commoner, who is going up and down the land denouncing Darwin and all his works, should read this book, though it is not likely he would be convinced of the error of his ways, notwithstanding the immense array of data in support of evolution

which it presents. This is the first of a series of four elaborately prepared volumes, intended to bring to the public at large a knowledge of the results and theories of modern science. The author is capable of the task, as shown by his previous work, and as well exemplified in the text at hand. The bulk of the present volume is taken up with a presentation of the theory of evolution of organized beings, the author being evidently an implicit believer in the same. The first fifty pages are devoted to a summary of the modern investigations in astronomy, after which nearly two hundred pages are devoted to an exposition of the nature and causes of evolution. Man's poor relations are owned without hesitation, and as the present storm of opposition to the teaching of evolution in schools and colleges is most intense in reference to the "descent (or ascent) of man," Professor Thomson's views lead to the storm-centre. Mr. Bryan has said that he would have no particular objection to the teaching of the principles of evolution as applied to rocks and plants, but for the danger that such views would be extended to the higher organisms. Scientists may smile at such statements, and the reviewer may be criticised for deeming them worth notice, but, as a matter of fact, a large mass of the public, even the somewhat enlightened public, is easily aroused by charges that a scientific doctrine may threaten prevailing faiths, and Mr. Bryan is a powerful speaker, who has an immense vogue throughout the United States. An act, which he actively advocated, to forbid the teaching of "Darwinism, atheism, agnosticism, and evolution as applied to man" failed by only one vote in the lower house of the Kentucky legislature, and the propaganda is going on continually.

The challenge is made in the title of chapter V, "The Ascent of Man." Darwin's "Descent of Man" is credited with practically closing the discussion in favor of a direct relation between human beings and apes. It is not necessary to take up the arguments in detail. They have been before the world for many years and set forth in many phases. Professor Thomson, in common with most naturalists, emphasizes the *resemblances* of the existing apes to man, while the opponents of the evolutionary view emphasize the *differences*. It is, therefore, difficult to bring the disputants to a common ground. The discussion has been complicated by some leading naturalists making rash statements. Such are claims for restoration of heads of primitive man in which it is to be feared that the artist has been allowed too free play.

Turning to the book in hand, one notes at once a sumptuous make-up that will go far toward securing popularity. This is a wise plan; the general reader must be drawn to scientific literature by attractive setting. If the propaganda is to be conducted by lectures, these must be well illustrated by experiments or lantern demonstrations; if by books, these must be well supplied with pictures. The high development to which both ordinary illustrations and those in color have been brought in late years, renders it easy to cater to the popular desire. The present work meets all requirements in this respect. The illustrations are numerous and of high type. One can almost read the book by looking at the pictures. The type is large and clear, making it easily read, and the printing and paper first-class. The text is well written, shows a large amount of research, and an earnest desire to present the facts, though it is not possible to overlook the evidence of the

author's bias towards the most advanced of the modern views. He is not to blame for this, for contact with organized structures, especially in their natural associations, leads an analytic and enfranchised mind in only one direction, namely, that a "blood relationship," so to speak, exists between them. Evolution does not necessarily involve the belief that all living organisms are of common ancestry; there may have been independent origins of life, but the similarity of plan seems to have no other explanation that the scientist can accept except the influence of heredity modified by environment.

In reading books of this type, the question arises as to whether they accomplish the purpose for which they are produced. There is a demand for them on behalf of a limited portion of the public, but the masses remain untouched by the methods and results of science. A part of the effort at the popularization of science is due to the desire to make the path of the research worker more easy, to secure a wider interest in his labors, and to justify the appropriation of public money for purely scientific investigation. Yet, even the most valuable results do not influence the minds of the great mass of the community, which clings obstinately to its folk-lore and superstitions. It is interesting to place Doctor Thomson's book alongside of the recent work of Seligman on the "Evil Eye," in which several hundred pages are devoted to setting forth the distribution both in space and time of this terrible superstition. The truth is that the mass of scientific research flows over mankind with about the same effect that the water of a stream flows over the pebbles scattered along its channel, disturbing a few, smoothing and rounding others, but leaving the general conditions comparatively unchanged. "Constant dropping will wear away the stone," but investigation shows that turbid water is most effective in this respect, and writers of fiction and poetry can swerve men more easily than can the scientist. Nevertheless, books of this class have their value, and the one now in hand is one of the best of the recent efforts to give the "man in the street" some knowledge of the accomplishments and theories of modern science.

HENRY LEFFMANN.

DYES CLASSIFIED BY INTERMEDIATES. B. R. Norris Shreve, in collaboration with Warren N. Watson and A. R. Willis, Chemists, U. S. Tariff Commission. 631 pages, including a glossary of dye-names, formula index and a key-list to Schultz numbers, 8vo. The Chemical Catalog Company, New York, 1922. $10.00 net.

The dye problem is the most complex one in the relations of chemistry to economic conditions. The enormous growth of the industry along comparatively narrow chemical methods, and yet the great variety and importance of the products make a comprehensive statement of even the leading features very difficult. The war brought to the notice of the world, and indeed, to some nations, very forcibly and painfully, the wide field that the applied chemistry of the tar-products covers. The prominence that colors and explosives have had of late years has thrown into the shade the other derivatives of the cyclic compounds, especially the medicines. While it is unfortunately true that a great many of the so-called synthetic medicines that Germany poured onto the world during the past quarter of a century were of little real

value, indeed, often worthless, sometimes harmful, yet a few, such as the remedy first announced as "606," have been valuable additions to therapeutic armament. Then we have the fairly numerous and useful photographic developers, among which metol and hydroquinone are easily first in favor. Lately a color, phenosafranin, has found a useful application in photography, as it has the power to diminish the sensitiveness of the exposed plate without appreciably affecting the latent image.

The work in hand is limited to the dyes, and is mainly intended to furnish a classification according to the intermediates from which they are derived. This method is based, according to a statement in the preface, upon the experience of the factory; it does not, at first thought at least, seem to the general chemist as very satisfactory, but it is not infrequent that the manufacturer has a decidely different viewpoint from the user or the analyst. It is, however, not to be doubted that the book will be useful to the research chemist. It contains a very large amount of information well arranged. There is much information as to the importation and home manufacture of the materials. These data will be of service in elucidating some of the complex issues that have arisen in connection with the efforts to secure strong protection to the infant dye industries in this country. Much feeling is apparent in the matter; lately in Congress some members nearly came to blows. The strongest argument for national development of the dye industry is its close relation to the production of modern explosives, asphyxiating gases and other accessories of "Christian" warfare, as it is now often called. This is not the place to enter on a discussion of the economic phases of the question, the real interest being in the character of the book under review.

The work is very comprehensive, but naturally not exhaustive; the field is too large for the compass of even several volumes. The intermediates are arranged alphabetically, with abundant cross references, and with synonyms. The nomenclature is not exactly that of *Chemical Abstracts*, but the names used by that publication are given also, and the principal formulas are listed in a convenient manner, so that the use of the *Chemical Abstracts* will be made easy. A formula index to the intermediates is also furnished and a reference to Schultz's numbers. Many structural formulas are given, and it is gratifying to see that the correct method of using the benzene ring is followed.

Turning over the pages of the book one is almost awe-struck by the multiplicity and complexity of even the intermediates, and realizes the service in interpreting their structure that was rendered by Kekulé's suggestion of the benzene ring. A further emotion of awe, or even terror, seems to be capable of being aroused if one was to attempt to develop a comprehension of the character of the molecule of one of the more complex intermediates so as to include the ideas of atomic and molecular structure now so extensively promulgated by the physical chemists.

During the last eight years, the attention of American chemists has been strongly directed to the theory and applications of the coal-tar derivatives. Much has been accomplished towards securing independence of Germany. Many colors are now made of as good quality as those from east of the Rhine, and brilliant success has also attended American efforts to produce

certain medicines, but the references to the literature still show how large is the world's indebtedness to Germany, and German chemists may still hold important secrets in all the departments of the utilization of tar.

The book is an excellent piece of work, shows the high mechanical execution of the publishing house that issued it, and the labor that the author and his collaborators have given to its production.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 125. General Classification of Instruments and Problems including Bibliography, by Mayo D. Hersey. 22 pages, quarto. Washington, Government Printing Office, 1922.

This report is intended as a technical introduction to the series of reports on aeronautic instruments. It presents a discussion of those subjects which are common to all instruments. In the first place, a general classification is given, embracing all types of instruments used in aeronautics. The arrangement of information dealing with these various instruments throughout the reports is then briefly indicated as a guide to the reader. Finally, a classification is given of the various problems confronted by the instrument expert and investigator. In this way the following groups of problems are brought up for consideration: First, those of mechanical design; second, human factor; third, manufacturing problems; fourth, supply and selection of instruments; fifth, problems concerning the technic of testing; sixth, problems of installation; seventh, problems concerning the use of instruments; eighth, problems of maintenance; ninth, physical research problems. This enumeration of problems which are common to instruments in general serves to indicate the different points of view which should be kept freshly in mind in approaching the study of any particular instrument.

Report No. 130. Oxygen Instruments, by F. L. Hunt. 23 pages, illustrations, diagrams, quarto. Washington, Government Printing Office, 1922.

This pamphlet contains an account of the physiological effects of the lack of oxygen at high altitudes and the amounts required to be supplied artificially to aviators under normal conditions of flight. It describes in detail the various types of aircraft oxygen apparatus which have been designed and used not only in this country, but also in England, France, and Germany. Instruments of both the compressed oxygen and liquid oxygen type are considered.

Methods of testing oxygen apparatus used at the Bureau of Standards are also fully described and the quantitative results of tests of sample instruments of different types are given.

Report No. 144. The Decay of a Simple Eddy, by H. Bateman. 7 pages, quarto. Washington, Government Printing Office, 1922.

The principal result obtained in this paper is a generalization of Taylor's formula for a simple eddy. The discussion of the properties of the eddy indicates that there is a slight analogy between the theory of eddies in a viscous fluid and the quantum theory of radiation. Another exact solution of the equations of motion of a viscous fluid yields a result which reminds one of the well-known condition for instability in the case of a horizontally stratified atmosphere.

PUBLICATIONS RECEIVED.

Dyes Classified by Intermediates: Dyes tabularly arranged under each intermediate, with statistical and other data for both dyes and intermediates. Glossary of dye and intermediate names alphabetically arranged by R. Norris Shreve, Consulting Chemist in collaboration with Warren N. Watson and A. R. Willis, Chemists, U. S. Tariff Commission. 631 pages, 8vo. New York, Chemical Catalog Company, Inc., 1922. Price, $10.

Catalytic Action, by K. George Falk. 172 pages, 8vo. New York, Chemical Catalog Company, Inc., 1922. Price, $2.50.

The Outline of Science: A plain story simply told. Edited by J. Arthur Thomson, Regius Professor of Natural History in the University of Aberdeen. In four volumes, volume one. 296 pages, illustrations, 40 colored plates, quarto. New York, G. P. Putnam's Sons, 1922. Price, $3.75 per volume.

Electrical Engineering Testing: A practical work on continuous and alternating currents for second- and third-year students and engineers, by G. D. Aspinall Parr, M.Sc., M.Inst.E.E., A.C.G.I. Fourth edition revised and enlarged. 691 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1922. Price, $8.00.

Électricité atmospherique, par B. Chauveau. Premier fascicule. Introduction historique. 90 pages, 8vo. Paris, Octave Doin, 1922. Price, 10 Francs.

Rayonnement et Gravitation, par Felix Michaud. 63 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 6 Francs.

L'Erreur de M. Einstein l'inacceptable théorie, L'Ether et le principe de relativité, par Marcelin Dubroca. 49 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 4 Francs.

Éther-Électricité-Relativisme, par le General Chapel. 40 pages, 12mo. Paris, Gauthier-Villars et Cie., 1922. Price, 2 Francs 50.

Les Preuves Astronomiques de la Rélativité, par E. Esclangon. 27 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922.

[The theory of relativity leads to a certain number of astronomical inferences which are at present under consideration. The author decides that the confidence which is generally given to these data is still not wholly justified, but expects that solutions of the problems will be obtained in the near future.]

National Advisory Committee for Aeronautics: Technical Notes No. 96, Notes on Propeller Design, IV. General proceeding in design by Max M. Munk. 9 pages, plate, quarto. No. 98, Notes on the Design of Latticed Columns Subject to Lateral Load, by Charles J. McCarthy. 18 pages, illustrations, diagrams, quarto. No. 99, Notes on the Standard Atmosphere, by Walter S. Diehl. 9 pages, quarto. No. 100, Theory of the Slotted Wing, by A. Betz. 13 pages, illustrations, quarto. Washington, Committee, 1922.

U. S. Bureau of Mines: Bulletin 207, The Analytical Distillation of Petroleum and its Products, by E. W. Dean, H. H. Hill, N. A. C. Smith and W. A. Jacobs. 82 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1922.

The Piezo-electric Resonator, by W. G. Cady, Wesleyan University, Middletown, Connecticut. 32 pages, illustrations, 8vo. Reprinted from the Institute of Radio Engineers, volume 10, April, 1922.

CURRENT TOPICS.

Reconstruction Hospital. (*Industrial Management*, June, 1922, p. 362.)—Care and after-treatment of the 1,000,000 or more yearly cases of injuries received by workers while at their trades are problems giving growing concern to leaders of industry all over the United States. The condition presents both human and economic factors. Not only has the workman a right to the most modern and scientific treatment of his injury, but the industry also, no matter what it is, can ill afford to face a condition wherein he passes a long convalescence and in many cases becomes a cripple unable to take his place at the work he likes and for which he has been trained.

Various of the great industries had worked out plans of many sorts for local care and rehabilitation of their own industrial casualties before the war, and since then have applied the discoveries and lessons learned during that period to their local problem in so far as they can.

Perhaps the most sensational advances have been made in the creation of a series of strange gymnasium appliances, which give the patient by mechanical means an easy road to the recovery of all his lost control over stiffened joints and partly paralyzed muscles. All of these things take a big hospital equipment and the services of a specially trained staff of specialists. The modern science of human physical rehabilitation is new in that it has only since the war been developed to a stage where it has been possible for a whole hospital to specialize intelligently and successfully in making injured workers, who have been "cured" into alert, active, efficient men who can go back to their jobs with confidence and without pain.

One difficulty in the spread of this work is the lack of trained staffs and of nurses educated in dealing with the reëducation and rehabilitation of men who have progressed beyond the scope of a general hospital. In the matter of diagnosis alone the surgeons at the Reconstruction Hospital in New York City put the patient through a searching examination that sometimes employs the services of many specialists aided by advantageous electrical and mechanical agencies.

From this hospital they send the industrial casualty back to a job and his opportunity to again support himself and family in from one-third to one-half the time he would otherwise need. Often they send him back in perfect command of himself when he might otherwise have remained helpless all his life. R.

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